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THE COLLOID AND SURFACE CHEMISTRY
OF ALLOPHANE

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ABSTRACT

The predominant clay mineral in many soils formed on weathered volcanic ash in the central and northern part of the North Island of New Zealand is the amorphous aluminosilicate allophane. Although it can be obtained cheaply, allophane is the only common clay mineral not yet exploited commercially. This may be because large deposits of it only occur in a few areas of small extent on recent andesitic and rhyolitic parent material. These areas are usually remote from the industrial areas of the world. Allophane has been studied by soil chemists who have been concerned with its influence on the properties of soils. Their work suggested that allophane has unusual ion exchange and colloidal properties but much of the surface and colloid chemistry of allophane was not well understood. The aim of this project was to investigate the properties of allophane with the view of developing commercial uses and also to understand better how it might behave in the natural environment.

Amongst the physical properties determined were density, surface area and particle size distribution, for which a new centrifugal method was developed. From these properties it was shown that allophane is extensively hydrated and has a much larger surface area than could be associated with its external surfaces, confirming that it has a large internal surface.

The surface charge of an allophane sample was determined by potentiometric titration; its point of zero charge was found to be below pH 5. However, determination of the surface charge below pH 6 was

complicated by the dissolution of aluminium. The isoelectric point of the same material, as determined by electrophoresis, was near pH 6. This is about 3 pH units higher than for clay minerals such as kaolinite, halloysite and montmorillonite and so allophane is one of the few natural colloids which is neutral or positively charged at soil pH's. The difference between the isoelectric point and the point of zero charge was due to the influence of the two different surface components; aluminosilicate, which tends to be negatively charged at near neutral pH, and aluminium hydroxide which tends to bear a positive charge under the same conditions. Dissolution studies showed that allophane derived from Tirau soil had aluminium in a state similar to that in aluminium hydroxide gel; that from Ohaupo soil had aluminium in a less soluble form but it was still more readily available than that generally associated with halloysite. Similar studies suggested that the iron found with allophane might exist as a separate and discrete phase. Some support for this was obtained from the uv spectra of allophane suspensions where weak absorbance bands were observed which coincided with those of colloidal iron (III) hydroxide.

The "site-binding" model for ion adsorption at the hydrous oxide/aqueous interface was studied and it was developed and extended to cover multivalent cations, mixtures of cations, and cation adsorption in the presence of a slightly soluble metal hydroxide. The predictions made of the expected selectivity, selectivity changes with pH, and the effect of the presence of aluminium hydroxide on the adsorption of cations by a hydrous oxide were substantiated by the results of a study of cation adsorption by allophane. Cation adsorption was enhanced by increasing the pH. It was generally greater for cations of greater ionic charge, radius, and ease of hydrolysis. The selectivity shown by allophane between any two cations was found to vary with pH; at low pH the more favoured ion was that with the larger radius and lower charge

but with pH increase the selectivity changed in a regular manner to favour small highly charged ions. The selectivity sequence at pH 4.0 was $\text{Pb}^{2+} \gg \text{Tl}^+ > \text{Sr}^{2+} \sim \text{Co}^{2+} \sim \text{K}^+ > \text{Ca}^{2+} > \text{Na}^+$ but at pH 6.0 it had changed to $\text{Pb}^{2+} \gg \text{Sr}^{2+} \sim \text{Co}^{2+} > \text{Ca}^{2+} > \text{Tl}^+ > \text{K}^+ > \text{Na}^+$. Monovalent thallium was found to bind more strongly, at lower pH, than any divalent species except hydrolysed lead. In much of its surface and colloid chemistry allophane behaves as a hydrous oxide. This is particularly evident from its interactions with ionic materials and from its colloid properties, i.e., its flocculation and electrophoretic mobility.

Because of possible use in water treatment and pollution abatement the interactions of allophane with biopolymers such as protein and ribonucleic acid were studied. It was found to bind both strongly. The strength of adsorption of these was controlled by the pH and maximum adsorption occurred at the polymers isoelectric point. Viruses were shown to behave like proteins in their interactions with allophane; very efficient removal from suspensions of low concentration was shown to be possible.

To investigate whether allophane could have any effect on the nutrient state of local lakes, studies were undertaken of the interactions of allophane with suspensions of the small green algae, *Chlorella vulgaris*. It was shown that these algae could be successfully flocculated by small amounts of allophane; in a suspension of 10^6 cells per ml the first signs of extensive floc formation were visible after the addition of only 2 μg of clay per millilitre. The efficiency increased with increasing allophane concentration. The flocculation also proceeded at pH 7.2 where each colloid was separately stable. It was shown microscopically that the allophane was acting as a bridge between the algal cells to which it became bound, probably by the polysaccharides of the cell slime layer.

The interactions of allophane with phosphates, biopolymers and microorganisms indicate that when it was able to enter lakes and rivers as a consequence of erosion, either naturally or assisted by man, it was capable of retarding, or even reversing, eutrophication.

As a result of its high isoelectric point the colloid and surface chemistry of allophane differs from that of the other common clay minerals. The major differences are its greater ability to adsorb anionic materials whilst retaining a high capacity for cations, the ease with which it can be flocculated from neutral suspensions when the other clay minerals form stable sols, and its ability to flocculate stable negatively charged biocolloids. On the basis of these properties, and its high surface activity, allophane shows promise for use as an adsorbent and flocculant for effluents from such industries as slaughterhouses, canning factories, geothermal power stations and sewage treatment works (particularly those using oxidation ponds growing algae).

A sound chemical case exists for investigating the use of allophane for effluent treatment at the pilot-plant stage. From this the possibility of utilising some of the billion tons of readily accessible allophane in New Zealand could be decided.

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INTRODUCTION

In the past million years large areas of the North Island of New Zealand have been liberally coated by ash showers from volcanic eruptions. These contained pumice and finely divided volcanic glass which have weathered to form the amorphous clay mineral allophane. Allophane is a poorly structured aluminosilicate coated to variable degrees with the hydrous oxides of aluminium and iron (III).

In the Waikato, Taranaki and on the Volcanic Plateau extremely productive farmlands and forests have been developed on the soils derived from these ash showers. This development has been permitted by the unique properties conferred on the soils by the presence of the clay mineral allophane. This component has been responsible for making these soils friable, freely draining and resistant to consolidation during heaving grazing and so they are ideal for pasture farming.

Partly as a result of these properties, but more particularly because of its ability to fix phosphate fertilizer, an understanding of the structure and composition of allophane became necessary. Intensive study of some of its physical properties and of its interactions with phosphate have been particularly rewarding and these aspects of its chemistry are largely understood. Allophane has been shown to have a strong affinity for anions, a high internal surface area, a high isoelectric point and little regular structure. These properties set it apart from the other common clay minerals and are probably responsible for some of the pedological properties referred to above.

There are still many aspects of the colloid and surface chemistry of allophane that have been neglected. Some particular features include the influence of the labile aluminium hydroxide which is an integral part of the mineral, the rôle and form of the iron (III) component, the

nature of the cation retention sites and the effects of acidification. These may all be important not only in the soil but also in other environments where allophane might be found.

There is evidence to suggest that allophane may have important consequences in river and lake ecosystems. Its interactions with dilute solutions of simple salts and organic substances, and with suspended microorganisms may be of ecological significance.

There are some billions of tons of allophane distributed throughout New Zealand in a form from which it could readily be retrieved with little environmental disturbance. Unlike the other clay minerals which occur in large deposits of high concentration no commercial interest has been taken in allophane even though it has unusual properties and a high chemical reactivity.

The aim of this project was to investigate aspects of the colloid and surface chemistry of allophane with the view of further elucidating its structure and composition and its behaviour in the natural environment. Furthermore an understanding of the properties of this mineral was sought to determine what potential it has to permit exploitation in industrial processes.

CHAPTER ONE

AN INTRODUCTION TO THE COLLOID AND SURFACE CHEMISTRY OF CLAYS

1.1 Clays and Clay Minerals

Describing a material as a clay usually implies that it has plastic properties (i.e., it deforms under pressure when moist), is a natural material of fine grain size, and is essentially a hydrous aluminium or magnesium silicate. However, a number of interpretations are placed upon the term clay by scientists from different disciplines. Geologists consider clay to be sedimentary or rock particles with a diameter less than 4 μm regardless of origin. In the field of ceramics it is defined thus: "Clay is an earthy or stony mineral aggregate of hydrous alumina and silica, plastic when wetted sufficiently, rigid when dry and vitreous when fired at a sufficiently high temperature.", which emphasises the plasticity but only indirectly makes any reference to the particle size. In this work the term as used in soil science will be adhered to, i.e., clay is the finest and most reactive fraction of the soil with a maximum size of 2 μm . This is the optimum size for differentiation as most non-clay minerals tend to be present in the soils as larger bodies. It is also a suitable size in colloid chemistry as it includes those particles which can form suspensions stable with respect not only to flocculation but also, within reason, to sedimentation.

Expression of a substance as a mineral implies that it has a definite chemical composition or characteristic arrangement of atoms. A limited number of clay minerals have been found which are crystalline, sometimes poorly, and so they can be characterised by crystallographic techniques, notably X-ray diffraction (XRD).

1.2 Clay Mineral Structure and Composition

A very early concept of the nature of clay was that it was all basically one mineral, like kaolinite which could easily be obtained in a white (supposedly pure) state, and all other clays were impure forms of this. An alternate theory held that clays were amorphous colloid complexes, with little organised structure, of a mixture of hydrous silica, alumina and iron oxide. Later it was believed that clays were made up of a number of extremely small particles of a few minerals, a theory proved in the 1920s with the advent of crystallographic techniques notably X-ray diffraction (XRD). The structures of these minerals were predicted by Pauling¹ to be based upon a silicate layer organisation in which two units are involved. One of these is a sheet of silica tetrahedra joined at their bases to form a hexagonal network. The second is two sheets of oxygen atoms or hydroxyl groups close packed with metal ions occupying octahedral holes in the lattice. Combination of these two layer units in various ways gives the structures of all the common clay minerals.²

The simplest combination is the kaolinite structure which is one only of each of these units sharing a common oxygen sheet. Two-thirds of the oxygen atoms of this sheet are the apexes for silica tetrahedra whose bases are coplanar and arranged hexagonally. The third external oxygen sheet is all hydroxylic as are the remaining oxygens of the central sheet. To maintain electroneutrality two-thirds of the octahedral holes are occupied by aluminium to which all hydroxyl groups are bonded (fig.1.1). The structural formula of the unit cell is $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$.

In kaolinite itself these composite sheets are all linked together by hydrogen bonds from the hydroxyl groups of the outer octahedral layer to oxygen atoms of the silica groups of the neighbouring unit. The result of such aggregation produces the hexagonal plates so

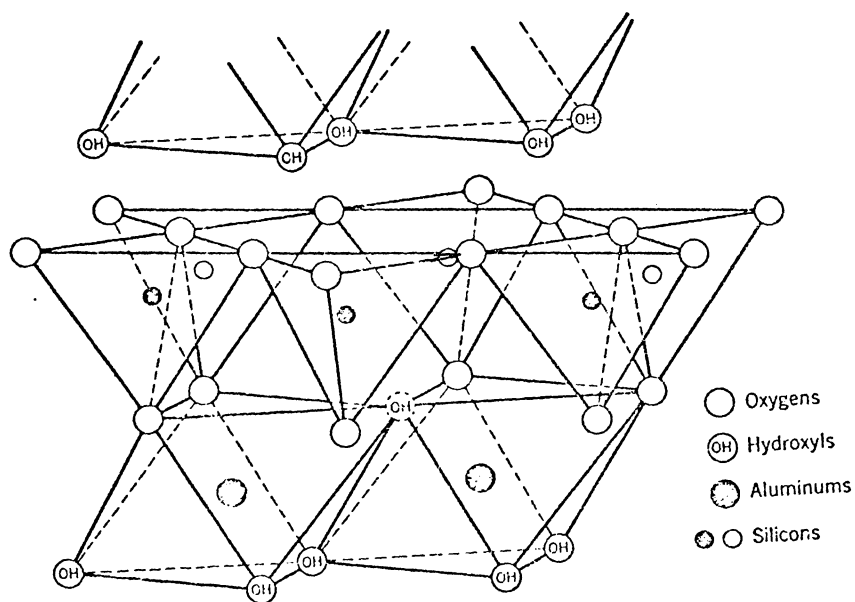


Figure 1.1. The structure of the kaolinite layer.
(From ref. 2.)

characteristic of kaolinite. Halloysite has the same structural basis as kaolinite but has a higher and variable water content. The most hydrated form has four water molecules per unit cell and these result in the cell thickness being 1.0 nm. Water is lost in two steps: initially about two molecules quite readily; complete hydration, which reduces the unit cell thickness to the kaolinite value of 0.7 nm, is more difficult and is irreversible. Halloysite generally has a tubular morphology although less crystalline forms are also known.

In montmorillonite, also known as smectite or bentonite, the octahedral layer is sandwiched between two silica layers and so it has four sheets of oxygen atoms of which only the two innermost bear any hydroxyl groups. The structural formula of the unit cell is $\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ where the water is adsorbed on the external surfaces (fig. 1.2). Generally substitutions occur within the lattice and these always unbalance the charge, e.g., magnesium (II) for aluminium (III), and aluminium (III) for silicon (IV). Further charges arise from vacancies within the octahedral layer. The nett negative charge produced is balanced by further cations either within the lattice or, more frequently, adsorbed at the surface. Both the water and the cations bind the lamellae together into plates or lathes. The final structure is dependent upon the substitutions. Adsorbed cations both from the external surface and from the interlamellar regions are usually exchangeable; if they are all the same, e.g., calcium, the clay is said to be in the calcium form or to be Ca-montmorillonite. Another important property of the smectites is that when they adsorb water after dehydration it enters the interlamellar region and they swell

Other clay minerals are formed by different substitutions within these lattices or by different arrangements of the tetrahedral silica and octahedral layers with various combinations of cations. Anions do

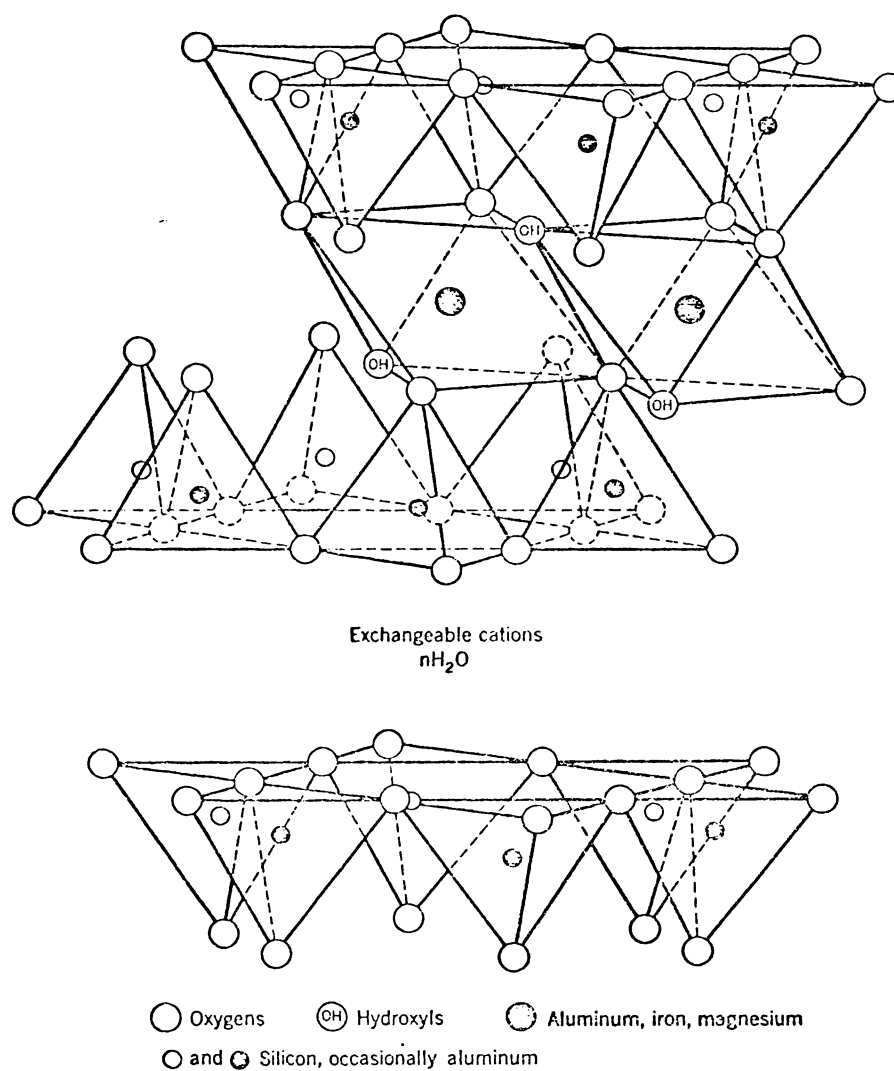


Figure 1.2. The structure of montmorillonite.
(From ref. 2.)

not play an important part in any of the common clay minerals.

The composition of clay minerals is commonly expressed in terms of the constituent oxides. For the materials discussed above these are given in Table 1.1.

Table 1.1 Composition of some Clay Minerals²

Mineral	percent by weight		
	Al ₂ O ₃	SiO ₂	H ₂ O
kaolinite	39.50	46.54	13.96
halloysite (7 ⁰ Å) (2H ₂ O)	39.50	46.54	13.96
halloysite (10 ⁰ Å) (4H ₂ O)	34.69	46.54	24.49
montmorillonite (H ₂ O free)	28.30	66.70	5.00

Naturally occurring clay minerals normally also contain adsorbed amorphous material, notably oxides, and variable amounts of substituted cations and quantities of other minerals. These make the compositions of Table 1.1 somewhat idealised.

1.3 Hydrous Oxides

The clay fraction of soils, which is their most reactive part, contains not only the clay minerals but also organic matter, ancillary minerals and amorphous materials. The hydrous oxides, which may be present as crystalline bodies but can also account for the greater part of the amorphous material, are usually those of silicon, aluminium, iron and manganese and may occur separately or in combination. Because of their small particle size, and hence large surface area, the presence of small quantities of them in the soil may have gross effects upon the soil properties. In particular their presence often dominates the

activity of ionic nutrients such as phosphate and trace metals.

The influence hydrous oxides have upon the soil structure is frequently a result of their coating the aluminosilicate minerals to a variable degree which greatly affects the electrical charge borne by these minerals, or by depositing on them to such an extent that they actually cement particles together.

1.4 Colloid and Surface Chemistry

Colloid chemistry is the study of the chemistry of small particles which have at least one dimension between about 1 nm and 1 μm . They are generally larger than large molecules but too small to be independent of the irregular bombardments of molecules of their supporting fluid. The movements induced in this manner are now known as Brownian motion after Robert Brown. He was the first person to suggest the existence of particles in the colloid size range after observing the random motions of pollen grains in water through a microscope. A direct result of this motion is that sedimentation of such particles is a slow process and in some cases, particularly when the suspenoid is fine or has a similar density to the supporting fluid, it may take years.

Dispersions of one phase of colloidal dimension in another phase are classified according to the combination. Aerosols are either solids, e.g., smoke, or liquids, e.g., fog, in gas; sols are solids in liquid, e.g., milk of magnesia (hydrosols are dispersions in water); emulsions are liquids in liquids, e.g., whipped cream; and gels are liquids dispersed in solids, e.g., jellies. A dispersion somewhat difficult to categorise is an aqueous protein solution which displays properties both of a solution and of a suspension.

As colloids are small they have large surface areas, often as high as $100 \text{ m}^2 \text{g}^{-1}$ or more, and so surface reactions play a large part in their chemistry. Surface chemistry involves the study of the processes that

occur in the boundary regions separating two phases. It is particularly concerned with adsorption which has happened to a material if its concentration in the interfacial region is different from its concentration in the bulk phase. When ions are adsorbed electrical charge separation can occur and an electro-chemical double layer forms. The thermodynamics of adsorption of many species have been investigated and theoretical models which predict their adsorption behaviour quite accurately in a number of cases have been proposed.

1.5 Some Properties of Hydrosols

The colloid chemistry of hydrosols, which include aqueous suspensions of the clays, the hydrous oxides, proteins, viruses, bacteria and to some degree small algae, can be categorised into four divisions:

- (a) preparation and characterisation of dispersions;
- (b) electrical studies of the solid/solution interface;
- (c) sol stability;
- (d) sol flocculation.

Preparation of dispersions is important in the formation of monodisperse colloids, i.e., colloids of a single material with a near uniform particle size, whilst their characterisation is associated particularly with their physical properties. Much information of particle size, shape and size distribution can be found from light scattering experiments although the associated mathematics are complex. The electron microscope allows visual observation of the colloid components from which the same information may be determined but to a different degree of accuracy and with a better appreciation of the true morphology and form of aggregation. The surface area of a colloid, in association with its particle size distribution, can give information of the porosity of the particles and, in conjunction with studies of

adsorption at specific surface functional groups, of the surface structure. The centrifuge is commonly employed by colloid scientists to separate particles of different size or density. It too gives information about particle size and size distribution as does the Coulter counter. This has the advantage that it measures particle volume and number directly although it is generally limited to particles of diameter greater than $0.7\text{ }\mu\text{m}$.

The field of electrokinetics, which is the study of the electrochemistry associated with the relative motions of electrically charged surfaces past liquids, has recently been found to be very useful for both practical determinations and theoretical considerations of surface electrical properties. The electrical properties of the interface of the sol and the liquid, especially the electrical charge and potential distributions that make up the electrochemical double layer, have important consequences in the properties of colloidal dispersions as they influence strongly the interactions between the colloid and other charged or polarisable bodies such as dissolved ions and molecules and other colloids. Modification of these properties can be made by variation of the concentration of electrolytes in the solution which may react directly with the surface and neutralise or enhance surface charge or modify the effective range of the charge distribution.

All particles have an inherent weak attraction arising from van der Waal's forces which are operative over only a very short dimension. The development of like surface charges on particles of a sol may result in the formation of sufficiently strong forces to overcome any van der Waal's forces and prevent particle aggregation. The sol is then said to be stable. Reduction of these electrical forces, or by-passing them by linking the particles via non-ionic or counter-ionic bridging molecules, results in the aggregation of particles into large units. These are not influenced by the thermal motions of the liquid and so phase separation

may occur. The sol is now flocculated. Stability and flocculation studies are primarily involved in preventing or inducing such aggregation by alteration of the solution conditions especially the electrolyte concentrations.

1.6 Colloid and Surface Chemistry of some Constituents of the Clay Fractions of Soils

1.6.1 Clay Minerals

In general the particles of clay minerals are less than about 2 μm and greater than 10 nm in diameter which means that they are colloidal. Because of their irregular shape and composite sheet stacking arrangements they may have apparent surface areas, measured by adsorption methods, much higher than might be anticipated for their size although this is dependent upon the strength of the binding between the sheets.

The surface chemistry of suspensions in aqueous solutions is dominated by the surface charge which is usually inherently negative from lattice substitutions and defects but which can be modified by acid/base reactions by any oxygen functional groups, particularly hydroxyl groups. In strongly acidic environments these groups may be protonated and so become positively charged whilst at higher pH, if surface groups are neutral or deprotonated, the surface bears a nett negative charge. Because of this variability with pH clearly all ionic interactions will be pH dependent. Thus cation adsorption will tend to increase and anion adsorption will decrease, with increasing pH. Minerals with inherent negative charges from structural substitutions and defects must of course always have some adsorbed cations associated with them be they organic, metallic or H^+ . Clays in the hydrogen form (H^+), are usually unstable and convert to the aluminium form on standing. In the aluminous clay minerals the presence of hydroxyl groups attached to only one aluminium atom at the sheet ends introduces regions of positive

charge in neutral suspensions as these groups are much more basic than the other surface oxygen groups. Electrostatic attractions between positive and negative regions induce aggregation of the plates in an edge-to-face manner which leads to the flocculation of suspensions of such materials. These flocs can be redispersed by blocking of the positive groups with small anionic bodies.

The heterogeneity of clay particles means that they are not ideal bodies for colloid studies. This arises because although a property can be measured for a whole particle unless all its surface is homogeneous the property cannot necessarily be related quantitatively to other phenomena meaningfully. Nevertheless, this does not detract from the value of determining electrophoretic mobilities, flocculation values and adsorption values, etc., for each specific material; it does mean they are not readily related to fundamental surface properties such as surface charge and any of the various electrical potentials found at the solid/aqueous interface.

1.6.2 Hydrous Oxides

The colloid and surface chemistry of hydrous oxides is important not only because they are reactive soil components involved particularly in the retention of ionic nutrients but also because they are extensively used industrial chemicals and they are used as model hydrosols as their surfaces are uniform and their size and shape can be controlled. In addition, the separation of various oxide ores by flotation methods is dependent upon the state of their surfaces. Furthermore, their general chemistry (their reactivities, thermodynamic properties, structures, etc.) is in many cases well documented. Sols of uniform size and shape have been very useful in theoretical studies of such colloid properties as light scattering, surface area, particle size and size distribution determinations. The oxides of silicon, aluminium, iron (III), manganese (IV) and titanium (IV) have been the most widely studied. They are all

common soil components and have extensive industrial and scientific uses. In addition they are all relatively insoluble at typical soil pH's, about $\text{pH } 5.5 \pm 1$, and in most natural surface waters.

As hydrous oxides are important commercial flocculants, their suspension stability, flocculation and adsorption characteristics have been closely examined and theories developed to explain the dependence of the above processes upon the parameters of the aqueous phase. It is known that both stability and flocculation are maximised in narrow pH ranges, the former when the surface is highly charged and the latter when it is near neutral. Flocculation is generally favoured by an increase in electrolyte concentration although often with multivalent ions a floc may be resuspended and then reflocculated with increasing ion concentration. Current theories of the adsorption of not only the cations and anions of the electrolyte but also of the aqueous proton and the hydroxide ion, can be adapted to explain most observed phenomena.

CHAPTER TWO

THE STRUCTURE AND PROPERTIES OF ALLOPHANE

2.1 Definition of Allophane as a Clay Mineral

The name allophane, taken from the Greek *allos* and *phainin* meaning "to appear" and "other" which is an allusion to the change in appearance from a glassy to an earthy state by dehydration on standing, was applied to material lining cavities in marl by Stromeyer and Hausmann³ in 1816. Since that time many materials have been described as allophane mostly on the basis that they were amorphous, although Ross and Kerr⁴ showed that a number of these geological samples were actually mixtures or were poorly crystalline. They proposed that the term allophane could be applied to all truly amorphous aluminosilicates regardless of composition.⁵ The definition suggested by White,⁶ that allophane is any amorphous substance that may be present in clay minerals and has an indefinite composition, recognises its heterogeneity and that oxides other than silica and alumina may be components but without making these two necessary.

Mitchell *et al.*,⁷ considered allophane to be naturally occurring, amorphous, mutual solutions of silica, alumina and water regardless of composition or, even more generally, any amorphous substance which may be present in clay minerals and which has an indefinite composition. Brown⁸ defined the composition as $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$ which recognises the importance of these three components but puts a constraint on the composition that has not been substantiated experimentally. Describing allophane as a hydrated aluminosilicate mineral amorphous to X-rays and without ordered crystal structure similarly puts an unrealistic constraint upon its composition by the use of the term mineral. A more satisfactory definition (tentative) was put forward at an international seminar held in Japan in 1969⁹: "Allophanes are members of a series of naturally occurring minerals which are hydrous aluminium silicates of

widely varying chemical composition, characterised by short range order, by the presence of Si-O-Al bonds, and by a differential thermal analysis curve displaying a low temperature endotherm and a high temperature exotherm with no intermediate endotherm." de Villiers¹⁰ has pointed out, however, that though this definition may be adequate for general descriptive purposes it does not give a basis for quantitative analysis.

The hydrous iron (III) oxides found with allophane in the soils derived from volcanic origins in New Zealand and Japan were considered by Milestone¹¹ to be an integral part. He defined allophane as a "colloid complex" of an amorphous hydrous aluminosilicate of widely varying composition, having a short range ordered structure of Al-O-Si bonds and a small amount of amorphous hydrous ferric oxide. This definition restricts application of the term allophane to materials containing iron (III) which would mean that other materials now recognised as allophane would be unclassified.

In this thesis allophane may be referred to as a clay mineral. It should always be borne in mind that the term mineral is being used loosely; mineral series would be more correct but it is less convenient.

2.2 Occurrence of Allophane

Although allophane was first found in voids in rocks it occurs most widely in soils where it was discovered by Seki¹² in 1914 in a Japanese volcanic ash soil. Since then it has been found in soils all around the world but the most extensive deposits are in soils derived from recent volcanic ash showers, especially in the Pacific basin. In such soils it may be the only clay constituent of significance although it frequently is accompanied by halloysite and imogolite.

The earliest report of its presence in New Zealand was by Henderson and Ongley¹³ in 1925 who were studying ash beds in the Mairoa area near Te Kuiti. In the fifties it was shown by Birrell and Fieldes¹⁴ to be an

important constituent of soils developed on volcanic ash. Later it was found to be the major portion of the clay fraction of yellow-brown loams and yellow-brown pumice soils¹⁵ where it often occurs with crystalline clay minerals thought to be the final product of the weathering of volcanic glass.¹⁶ Two particular types of volcanic ash, and hence allophane, are recognised; that derived from rhyolitic volcanic activity and that from andesitic activity. Rhyolite and andesite are types of rock. The immature red and brown loams of New Zealand which are basaltic in origin have also been found to have allophane as their main clay constituent.¹⁵ Basalts weather to give, commonly, allophane and gibbsite which are found in young soils; these probably undergo further weathering as the older basaltic soils contain mostly crystalline clay minerals.¹⁷ An idea of the distribution of allophane throughout New Zealand can be found in *Soils of New Zealand*.¹⁸

The occurrence of allophane throughout the world is similar to that in New Zealand. It is predominantly associated with soils developed on volcanic ash beds especially in tropical and subtropical regions.^{7,19} It is also found frequently in basaltic soils.

2.3 Properties of Allophane

2.3.1 Physical Properties

Allophane from geological deposits often appears clear to white although it may be a wide variety of colours if elements other than those of the aluminosilicates are present. The occurrence of hydrous iron (III) oxides in the allophane of New Zealand volcanic ash deposits gives it a red-brown colour.

Allophane clay has a characteristic feel used in the field as an approximate guide by pedologists; when moistened, provided it has not

completely dried out, it has a "greasy but not sticky" texture.*

The electron microscope has proved to be a useful tool for identification of allophane as it has a distinctive "cauliflower head" or fluffy structure with no definite edges,²⁰ composed of units of about 5 nm diameter.^{14,21} The aggregates of these bodies are quite irregular and have numerous holes which contribute a large surface area, often of the order of several hundred square metres per gram, to the material.^{11, 22-24}

X-ray diffraction, which is a very useful technique for studying the crystalline clay minerals, has not been so useful in determining the structure of allophane as it is amorphous to them although some broad halos have been observed in some samples which may be correlated with regular atomic arrangements.²⁵ These halos were combined with differential radial distribution analysis to obtain some structural detail. The unit particle size from X-ray diffraction studies has been suggested as being less than 10 nm because the material appears amorphous,¹⁴ whilst small angle scattering experiments were interpreted in terms of bodies between 5 and 8 nm diameter.²⁶ Information about the coordination of aluminium in allophane has been obtained from X-ray fluorescence analysis and both tetrahedral and octahedral aluminous systems found.²⁵

Some idea of the bond types within clay minerals can be obtained from infrared absorption spectroscopy but the peaks in the spectra from allophane tend to be broad and featureless which is indicative of little definite structure.^{11, 16, 27, 28}

*This test is not infallible; it resulted in the incorporation of a finely divided halloysitic clay into this study. Although it was soon realised that the material was not allophane from its colloid properties, it was retained and used for a number of experiments partly as a reference material and partly to explore some aspects of the chemistry of this rather neglected mineral.

The differential thermal analysis curve for allophane shows two features, a broad low temperature endotherm from loss of water and a high temperature exotherm due to the transformation to mullite.^{6, 29} This property has been considered sufficiently distinct for it to be used in a definition of the material (see section 2.1).

2.3.2 Colloid and Surface Properties

The aqueous surface and colloid chemistry of allophane is in many ways like that of a hydrous oxide. It has a surface charge which varies almost linearly with pH, it adsorbs cations more strongly at higher pH than at low, and anions in the reverse manner, with no steps in the activity, i.e., a monotonic variation with pH.³⁰ The adsorption of most substances is concentration dependent, at least up to surface saturation. The adsorption of some ions is, however, so strong that they may become fixed or unavailable to plants in the soil.³¹ The two most important ions in this category are phosphate and potassium. Allophane also has properties as a cracking catalyst which, like the ion adsorption properties, can be associated with a marked surface acidity.^{30, 32} A number of organic compounds adsorb strongly onto allophane. Some do so so intensely that they cannot be removed completely with hydrogen peroxide.³⁰ Proteins also bind firmly and they may be protected to some extent from attack by enzymes. The enzymes themselves are also liable to be strongly adsorbed and denatured.^{33, 34}

As a further consequence of its surface structure allophane particles have no nett surface charge at a relatively high pH, commonly near pH 5 to 6, when compared with the other aluminosilicate clay minerals (except imogolite). Dispersion, which relies on the particles becoming highly charged from acid-base dissociation, can sometimes be achieved in both weakly acidic and basic suspensions.¹⁴ The electrophoretic and flocculation properties of allophane are also similar to the hydrous oxides.³⁵

Cooper³⁶ found strong adsorption interactions occurred between Tirau allophane and the bacteria *Escherichia coli* at pH's between their isoelectric points, i.e., between pH 6.0 and 2.8. The effective pH range of this interaction was narrowed by the adsorption of multivalent anions and increased by multivalent cation adsorption. The binding was claimed to be the result of electrostatic attraction and van der Waal's forces. Adsorption isotherms for pH greater than 5 showed a maximum of 10 cells per clay particle; the number required to completely coat each clay particle. At pH 4.5 a two-step isotherm was apparent with the maximum number of cells apparently adsorbed per clay particle approaching 15. The second isotherm was attributed to formation of flocs of *E. coli* alone; the cells were being bound by aluminium released from the allophane after acidification.

2.4 Structure of Allophane

Early ideas of the structure of allophane and amorphous aluminosilicates can be found in references 7, 11 and 37.

There is now a general consensus that in allophane there is a skeletal matrix of tetrahedral silica with a high proportion of these silicon atoms replaced by aluminium atoms which are then also four coordinate. This matrix has been described as both linear³⁷ and sheet-like.^{24, 38} With it is an external layer of octahedrally coordinated aluminium associated in a manner similar to that found between the tetrahedral and octahedral layers of kaolinite. Substitution of silicon by aluminium results in the presence of an internal negative charge which must be neutralised by other cations, particularly the octahedral partially hydroxylated layer. Surface protonation must also be considered to be an important charge neutralisation process.³⁷

Milestone¹¹ proposed that the surface of allophane could be represented by the structure shown in figure 2.1.

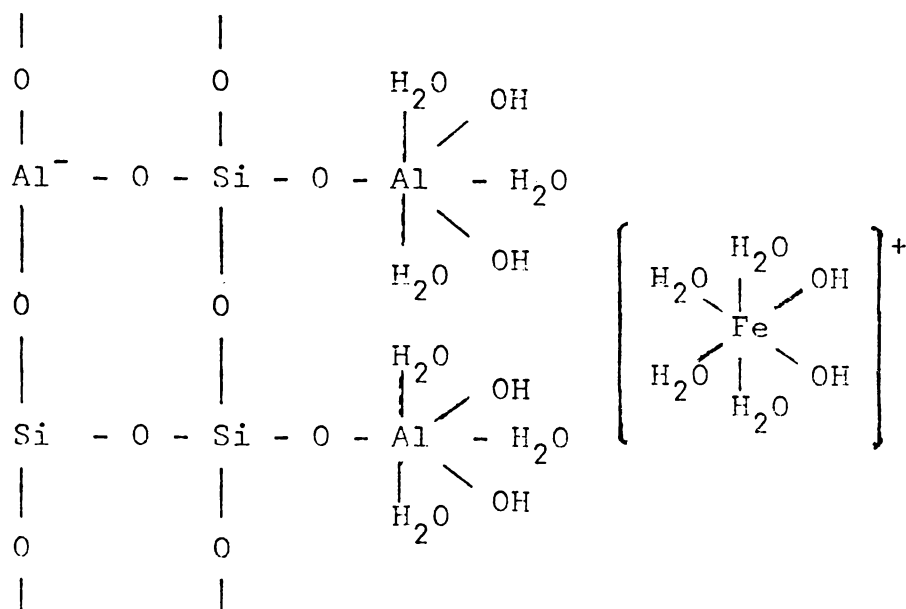


Figure 2.1. The structure of allophane proposed by Milestone.¹¹

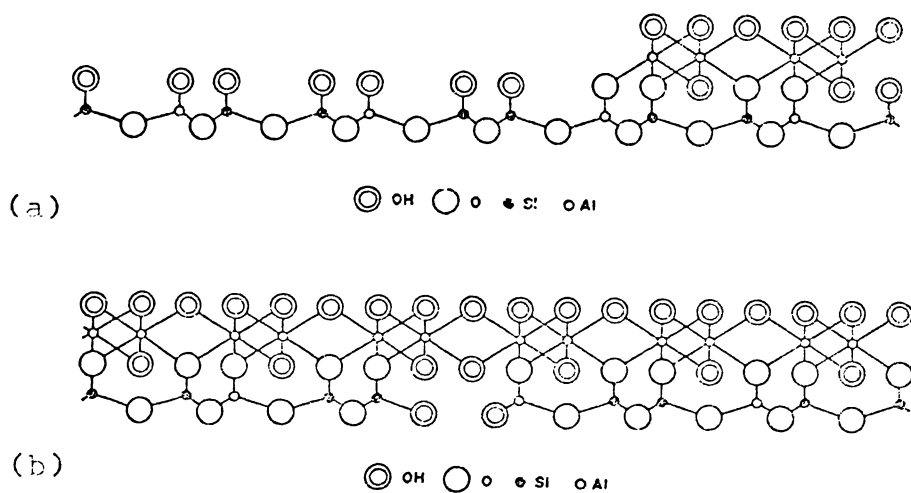


Figure 2.2. The structures of the end-members of the allophane series as proposed by Okada *et al.*²⁵

(a) $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$; (b) $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$.

Okada et al.²⁵ considered that the mineral series of allophane could be represented as having compositions lying between the two end members $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ and $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ which have structures incorporating not only Si-O-Al(IV), Si-O-Al(VI), Si-O-Si, Al(IV)-O-Al(VI), and Al(VI)-O-Al(VI) bonds (where the Roman numerals refer to coordination numbers) but also some vacant sites within the tetrahedral layer especially, which perhaps may contribute to a general loss of planarity. The structures of these two minerals are reproduced in figure 2.2.

No comment was made of the relationship between such sheets or whether they were distorted or curved. A variable degree of curvature or distortion would tend to make the properties of specific groups be scattered widely about the norm so that, for instance, infrared absorption bands would be quite diffuse. However, the smallest unit of allophane has been observed to be a sphere of about 5 nm diameter^{14, 21} and as the thickness of the sheet described by Okada et al.²⁵ will be similar to the thickness of the kaolinite lamella, about 0.7 nm, it could form the wall of these spheres which Kitigawa²¹ described as being hollow. Multilayer deposits of this structure, as found in the other clay minerals, might also be feasible provided charge neutralisation was total. However, no swelling occurs on hydration and so this morphology would be unlikely. If allophane does indeed exist as small spheres of about 5 nm diameter then the bodies described by Cloos et al.,³⁷ based upon a tetrahedrally coordinated $\text{Si}_{40}\text{Al(IV)}_{20}\text{O}_{110} \cdot n\text{H}_2\text{O}$ unit with a coating of polymeric positively charged aluminium hydroxide, are still too small to form these spheres.

Iron(III) is of much greater importance in allophane samples derived from volcanic ash soils than it is in those from geological origin. This is clearly borne out by the analyses of Milestone¹¹ and Okada et al.²⁵ who found mean contributions to the composition of 4.79% and 5.26% as Fe_2O_3 for five and four samples respectively for soil

allophane. Those reported by Weaver and Pollard³⁹ for six geological samples had a mean iron content of only 0.36% as Fe_2O_3 . In the soil samples the iron/aluminium ratio varied between 1:50 and 1:6, but as the structural properties did not vary greatly with this ratio, nor with the removal of the iron, it would be unlikely that the iron could be a significant structural component. Wada⁴⁰ in fact considered the iron to be of so little importance that he removed it before making morphological studies.

If the iron (III) is not a significant structural component then it must be present in some other position of which there are two possibilities. It could exist as either a discrete phase of hydrous iron (III) oxide or it could be adsorbed onto the aluminosilicate surface. If it covers a significant proportion of the surface of the allophane clay sized particles it would induce colloid properties associated with the oxide to the clay; in particular it would increase the tendency of the particle to have a nett positive external surface charge at near neutral pH's. In such a position it would also act as a binder between aluminosilicate bodies and so its removal would not greatly influence most properties of allophane other than its electrokinetics which would then approach those of the pure aluminosilicate itself.

The above structures suggest that polymeric aluminium hydroxide is also a major surface adsorbed species on some allophanes and so it too will temper the surface properties of the clay towards those of its own.

2.5 Properties of Soils Containing Allophane

The soils derived from volcanic ash showers in the Waikato and Taranaki regions are the most productive pasture-bearing soils in New Zealand. Furthermore, they have the highest nitrification activity (conversion of ammonium into nitrate) which is also generally higher than

soils overseas.⁴¹ To maintain high pasture yields, however, there is a large requirement for both phosphate and potassium. These soils are not sticky, they may have a waxy feel if the clay content is sufficiently high,⁴² and they can absorb large quantities of water without swelling. In the topsoil a large proportion of organic matter is common, often about 10% but sometimes as much as 20% by weight;¹⁸ stable mineral-organic complexes are frequently found.¹⁶

These soil properties can be related to the high content of allophane. The structure properties arise because in the soil the allophane is in a flocculated state and so the particles maintain an open structure rather than form a thick pug which would result if they were consolidated from a dispersed state. The absorption of water without swelling occurs because the liquid can be taken into the material's pores where, as it is not forcing layers of clay apart, it cannot cause significant morphological changes. These physical advantages of the soil for pasture growth are offset to some degree by its chemical requirements, the fixation and elemental deficiency problems, but good farming practices generally overcome these.

Whilst these soils are good for pastoral farming they are often unsuitable for base structures for roads as they become mobile under pressure if they are moist (they are plastic). Failure of road beds is a very expensive problem throughout much of the North Island and it is all too frequently associated with allophanic ash deposits. Stabilisation of base structures by incorporation of cement and lime (both cause greater interparticle interactions) has become a common highway engineering practice. Alternatively the beds giving this problem are removed.

CHAPTER THREE

THE PROPERTIES OF CLAYS SEPARATED FROM SOME WAIKATO TEPHRA

3.1 Origin and General Description

The clay fractions of three soils developed from geologically recent volcanic ash (the preferred term for all air-transported matter ejected from a volcano is tephra; ash being reserved for the less than 4 mm fraction) were separated. The soils from Ohaupo and Tirau have been used for general studies of New Zealand soils by the New Zealand Soil Bureau.^{18, 43} The horizon of the Mangawara soil investigated here has not previously been studied (but see Shepherd, ref. 44).

Ohaupo Silt Loam

This soil developed on Mairoa ash (rhyolitic) in rolling country under a rainfall of 130-140 cm per year. The sample, a yellow-brown silt loam, was collected from the C horizon, 60-80 cm, from a site at McGregors Road, Ngahinapouri.

Map reference: N.Z.M.S. 1 N65/769341

$\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio 1.69:1

$\text{Al}_2\text{O}_3:\text{Fe}_2\text{O}_3$ ratio 7.5:1

Tirau Sandy Loam

This soil developed on Tirau ash (andesitic) in easy rolling country under an annual rainfall of 130-150 cm. The sample, a yellowish-brown sandy loam, was collected from the (II)C horizon, 60-80 cm, from a site at Hetherington Road, Tirau. A full description of this soil can be found in *Soils of New Zealand* (ref. 18).

Map reference: N.Z.M.S. 1 N66/273253

$\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio 1.85:1

$\text{Al}_2\text{O}_3:\text{Fe}_2\text{O}_3$ ratio 9.0:1

Mangawara Clay Loam

The soil was taken from the K horizon, 200-230 cm, an early Hamilton ash (andesitic) about 0.5 million years old. The site at Welches Road, Mangawara, is easy rolling country receiving 120-140 cm rainfall annually.

Map reference: N.Z.M.S. 1 N56/763782

All samples were taken from roadside cuttings adjacent to pastures used for dairy farming.

3.2 Preparation of Samples

The soils collected in the field were kept in tightly closed plastic bags to retain moisture. When required they were passed through a coarse (2 mm) sieve which removed gross bodies. The clay fraction was separated by dispersion in the following manner.

About 200 g of sieved soil was suspended in one litre of distilled water, 30 ml of 30% hydrogen peroxide was added to oxidise organic matter and the mixture stirred for one hour. The pH was adjusted to near 9 with dilute sodium carbonate to assist dispersion (this step was unnecessary for the Mangawara soil as it dispersed in distilled water alone) and the mixture was stirred vigorously and boiled for two to three minutes. If the suspension had flocculated upon cooling, the supernatant was discarded and the sediment resuspended with stirring in fresh distilled water. When significant quantities of suspenoid were evident in the supernatant they were retained and the sediments further washed until free from clay. The liquids containing suspended material were then combined and the clay fractions separated from the larger bodies by sedimentation and centrifugation as described in section 3.7.

The clay suspensions produced in the above manner were concentrated either by high speed centrifugation in a Sorvall RC2-B high-speed centrifuge or by flocculation with sodium chloride. Working suspensions

were then prepared by resuspension in distilled water. If low electrolyte conditions were desired these suspensions were washed at the centrifuge until the desired concentrations were achieved. For most experiments the clay suspensions produced in this manner were suitable. They were maintained in suspension rather than as a dried powder as the processes that occur on dehydration are not necessarily reversible.²²

The concentration of clay in any suspension was initially determined from the dry weight of the residue of a suitable aliquot after oven drying at 110°C to constant weight.

When dry powder samples were required the suspensions were flocculated with acetone, washed twice with 50% aqueous acetone and then twice with acetone or ethanol and air dried. They were then ground lightly with a mortar and pestle to pass a 150 µm sieve and dried at 110°C for at least 24 hours or to constant weight.

3.3 X-ray Diffraction Studies

Powder samples of various fractions of the clays were scanned from 3 to 30° using a Philips 1130 X-ray system using Cu Kα radiation.

Both Tirau and Ohaupo clay samples were all essentially amorphous although the spectrum of Ohaupo clay showed weak, broad peaks at 0.73 and 0.44 nm which indicated a small amount of crystalline material. The Mangawara clay, however, gave strong peaks at 0.73, 0.44 and 0.36 nm, all indicative of metahalloysite. This mineral was also probably the crystalline material present in the Ohaupo clay. No significant differences were found between size fractions.

These results are consistent with the Tirau and Ohaupo clays being predominantly allophane and the Mangawara clay being halloysite.

3.4 Electron Microscopy Studies

Electron micrographs were recorded by both scanning and transmission electron micrography. For viewing by the transmission mode the clays were deposited from dilute aqueous suspension onto collodian film, evaporated to dryness in a vacuum desiccator and shadow cast with platinum. The samples for viewing in the scanning mode were deposited again from dilute aqueous suspension onto either brass stubs or filter paper, dried under an infrared lamp for five minutes and coated with a gold-palladium mixture. Some of the micrographs obtained are reproduced in Plates I to VIII.

The Tirau clay (Plates I and II) is similar to the sample of the same material shown by Fieldes¹⁶ (a clearer reproduction is shown in reference 45, Plate 34D) and illustrates the typical allophane characteristics; it is predominantly aggregates of widely varying sizes with no regularity and the very fine constituent particles that are free have a tendency to flocculate into platy aggregates.^{20, 46} Similar material from other soils of volcanic ash origin has been reported by, for example, Fieldes and Williamson⁴⁷ and Milestone.¹¹ The Ohaupo clay (Plates III to VI) also shows these characteristics, although the aggregates are quite irregular; this confirms its classification as allophane. A small amount of ordered material can be seen, particularly in the transmission micrograph, Plate VI, which because of its tubular nature suggests that it is halloysite, a supposition which concurs with the XRD analysis of this material. From these and other micrographs the allophane content has been estimated as near 90%.⁴⁸

The Mangawara clay (Plates VII and VIII) appears to be very similar to the allophanes but in addition to the apparently amorphous material it contains there are a large number of small spherical bodies of about 100 nm diameter and a high proportion of elongated bodies about 400 nm by about 70 nm. It is probable that the stick-like bodies are actually

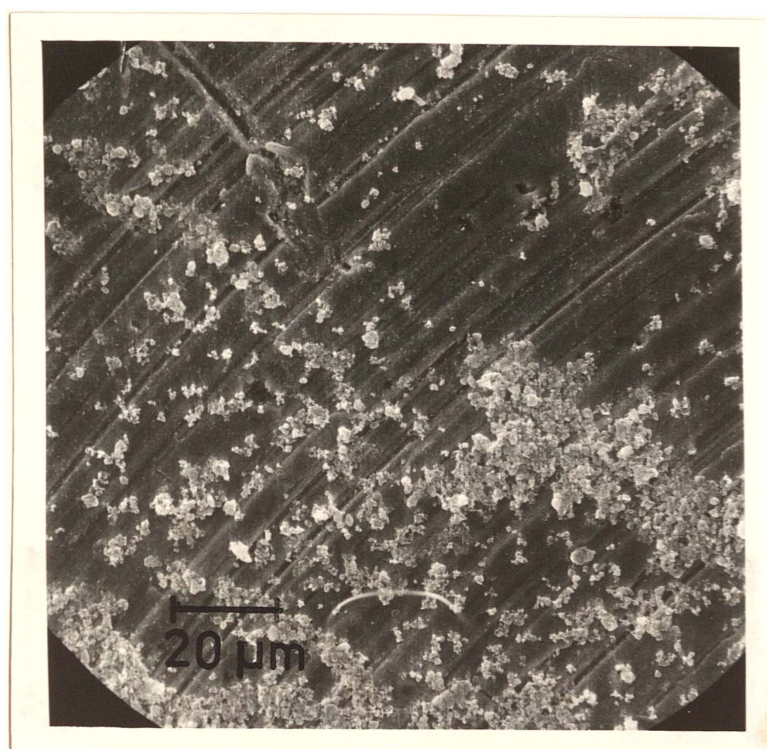


Plate I. SEM of Tirau clay. (x 660.)

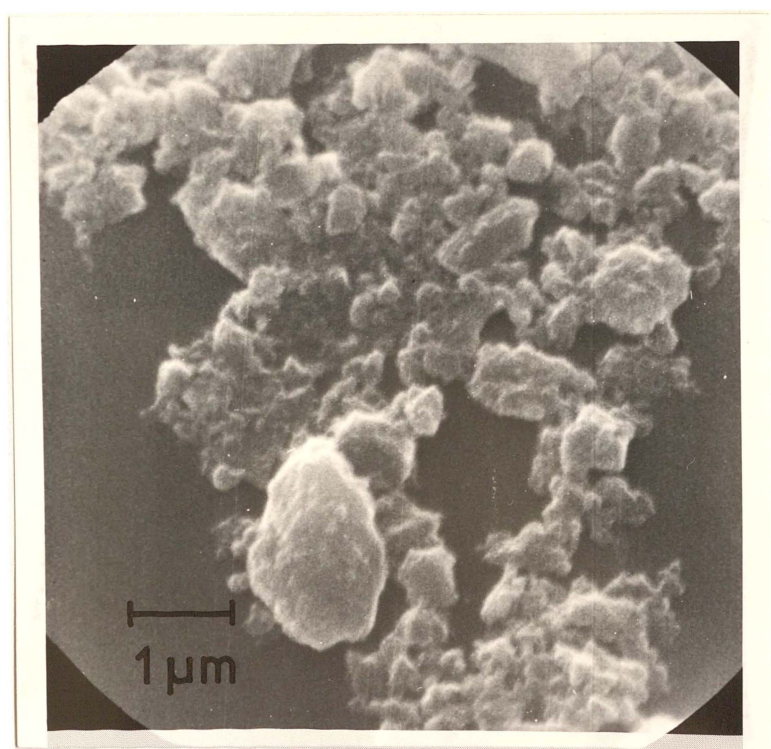


Plate II. SEM of Tirau clay. (x 13,000.)

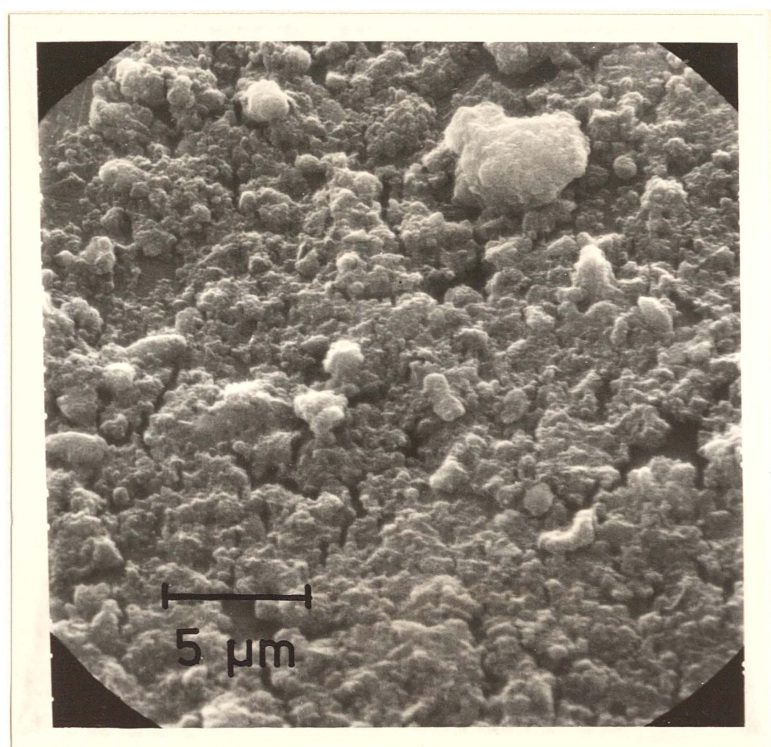


Plate III. SEM of Ohaupo clay. (x 3600.)

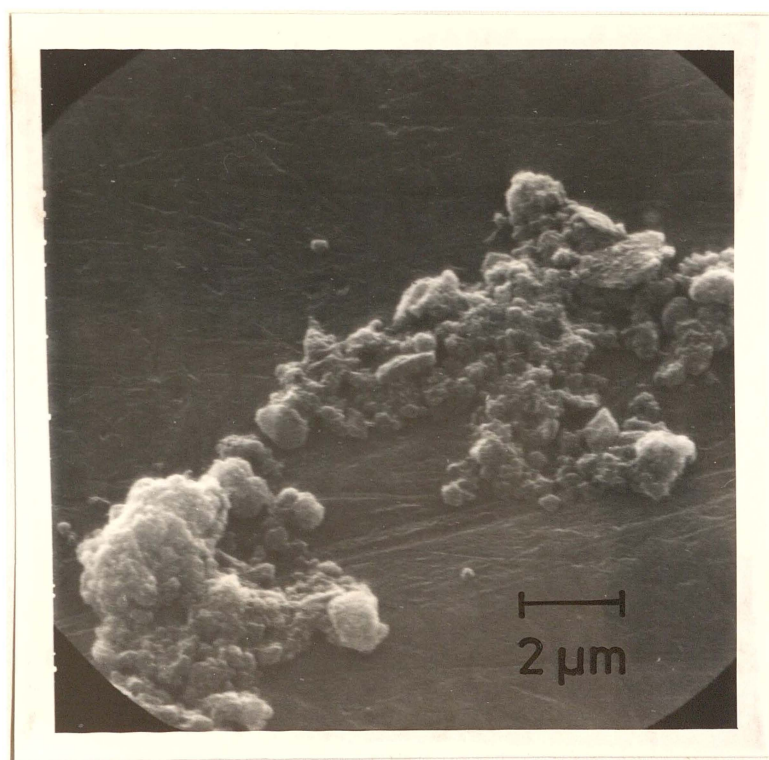


Plate IV. SEM of Ohaupo clay. (x 6,600.)

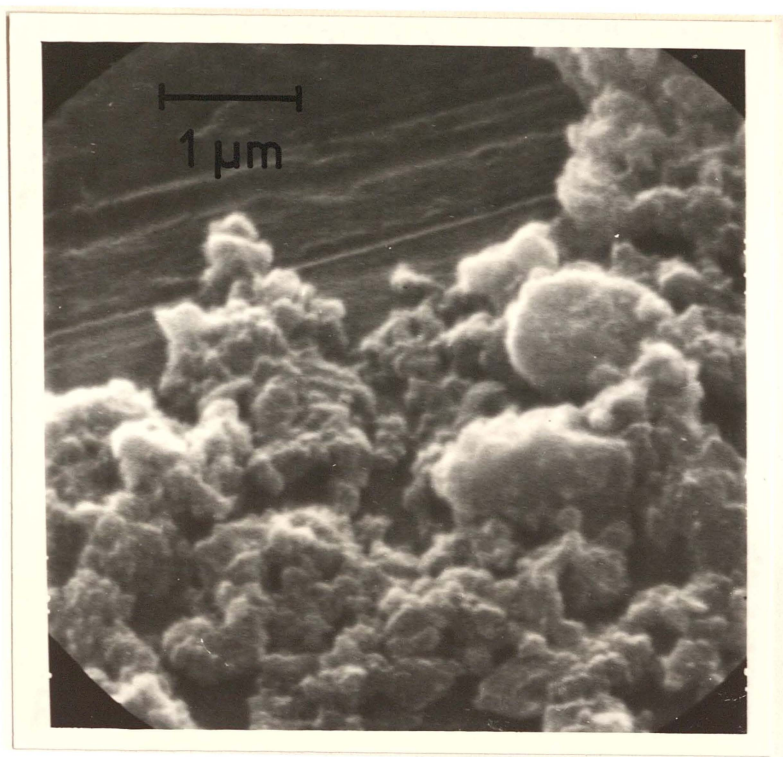


Plate V. SEM of Ohaupo clay. (x 18,000.)

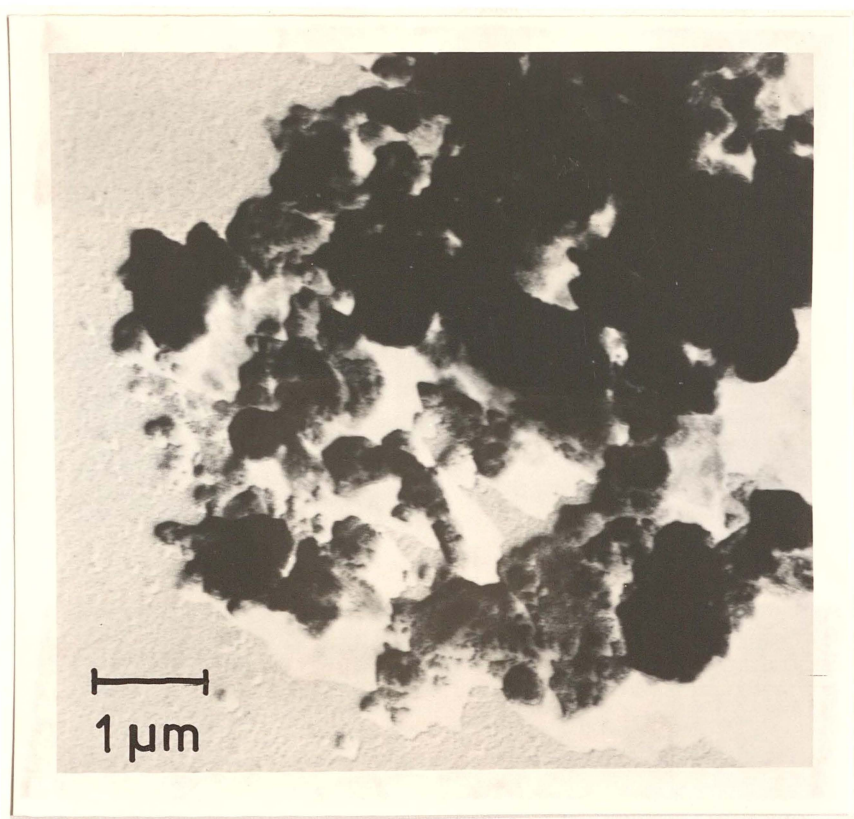


Plate VI. TEM of Ohaupo clay. (x 15,000.)

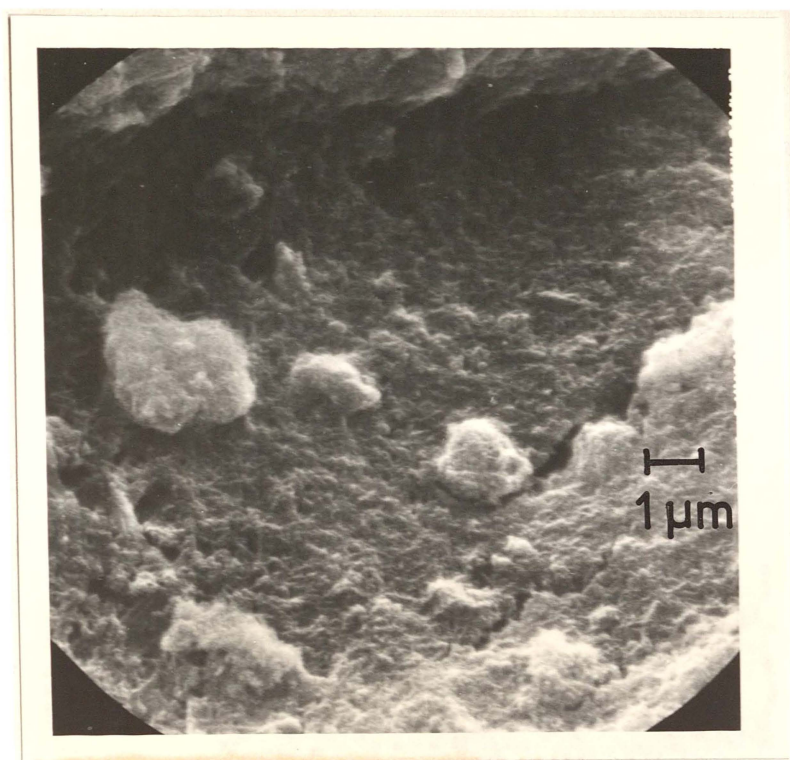


Plate VII. SEM of Mangawara clay. (x 7,200.)

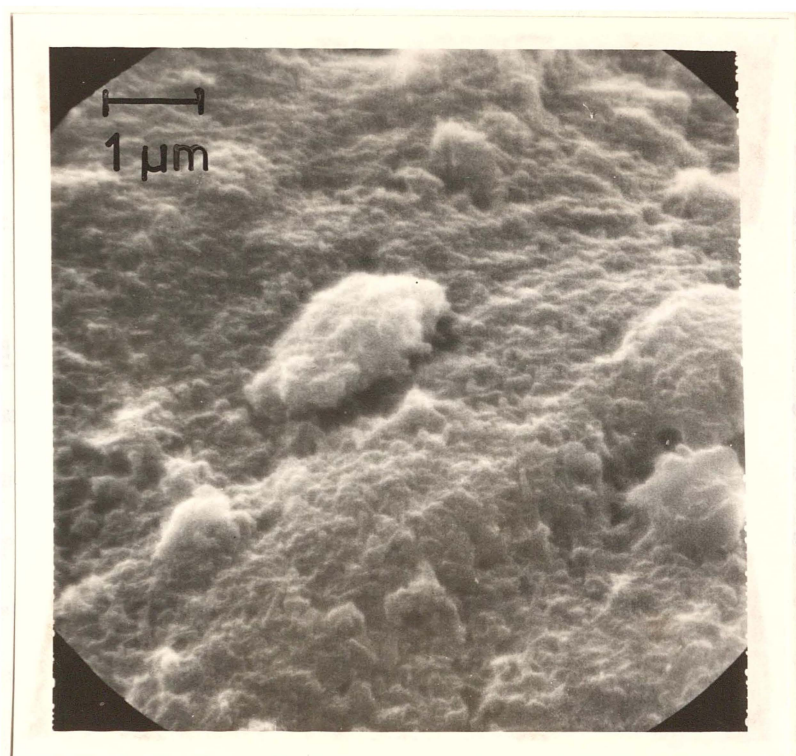


Plate VIII. SEM of Mangawara clay. (x 12,000.)

tubular, the most common halloysite morphology (for examples see refs. 16, 46, 47, 49). Halloysite is also known to have spherical forms. The very fine particle size and low degree of crystallinity associated with the two regular structures observed here will account for the low intensity and broadness of the peaks recorded in the XRD analysis of this clay.

3.5 Density Studies

3.5.1 Introduction

The density of a particle is an important factor in its sedimentation. A simple method of density determination is to prepare a dilute suspension of the solid in a liquid medium and subject it to a force which acts upon its mass. If there is a density difference there will be a tendency for the suspenoid to move under the influence of this force and so the greater the force and the greater the density difference the more pronounced the movement. If both densities are equal no movement will occur even when the system is subjected to forces as large as those found in the centrifuge. An advantage of the procedure outlined here is that only a few milligrams of material are needed.

3.5.2 Method

Small samples (about 50 mg) of clay, which had been dried at 110°C overnight were shaken in 5 ml of a mixture of bromoform and acetone of known density and centrifuged for 2 min at 2,000 rpm in a closed vessel. If the clay was not evenly dispersed through the liquid phase but accumulated at either the top or bottom of the vessel the density of the liquid was adjusted by the addition of either bromoform or acetone respectively and the procedure repeated. When the clay dispersed evenly through the liquid the density of the supporting liquid was determined with a pycnometer and this was also taken to be the density of the clay.

3.5.3 Results and Discussion

The densities of the three clays are presented in Table 3.1.

Table 3.1 Clay Densities

Clay	Density (g cm ⁻³)
Tirau allophane	2.16
Ohaupo allophane	2.30
Mangawara halloysite	2.55

These are not greatly different from the values of 2.3 g cm⁻³ quoted for allophane¹⁴ and 2.55 for halloysite.⁵⁰ Halloysite has a similar composition to kaolinite but is more hydrated and would be expected to be less dense (kaolinite has a density between 2.61 and 2.68).⁵¹ As the allophanes are more highly hydrated again their densities are somewhat lower. From Table 3.1 it might be expected that Tirau allophane is more strongly hydrated than the Ohaupo allophane. This expectation has been verified by thermal gravimetric analysis.¹¹ (The reduction in density by hydration arises because water is less dense than either alumina or silica, which are the major components of allophane. Such a situation is illustrated by the difference in density between boehmite, AlO(OH), and gibbsite, Al(OH)₃. These have densities of 3.01-3.06 and 2.38-2.42 g cm⁻³ respectively.⁵¹)

3.6 Surface Area Studies

3.6.1 Introduction

A number of the characteristics of colloidal species depend upon the specific surface area which can be determined by the adsorption of small molecules. A quantitative theory for gas adsorption was developed by Brunauer, Emmett and Teller⁵² (the BET theory) and this is frequently used in surface area determinations particularly with

nitrogen gas at its atmospheric boiling point, 77.4 K, and also with water at room temperature.

For a monolayer of adsorbate molecules on the surface of the adsorbent the BET equation has the form;

$$\frac{p}{x(p_o - p)} = \frac{p(c - 1)}{p_o x_{\max} c} + \frac{1}{x_{\max} c} \quad (3.1)$$

where p is the partial pressure of the adsorbate, p_o is the saturation (condensation) pressure, x is the number of moles of gas sorbed, and $x_{\max}$ is the number of moles of gas needed to form a monolayer. The constant c is defined by;

$$c = \exp\{(E_1 - E_L)/RT\} \quad (3.2)$$

where E_1 is the heat of adsorption of the first layer and E_L is the heat of condensation of the gas.

A plot of $p/x(p_o - p)$ against p/p_o will have a slope $a = (c - 1)/x_{\max} c$ and intercept $b = 1/x_{\max} c$ from which it can be seen that;

$$x_{\max} = \frac{1}{a + b} \quad (3.3)$$

The surface area is given by;

$$\text{surface area} = x_{\max} N \frac{(\text{crosssectional area of gas molecule})}{(\text{weight of sample})} \quad (3.4)$$

The crosssectional area of water⁵³ is 0.105 nm² and of nitrogen,⁵² which is somewhat larger, is 0.162 nm². N is Avogadro's number.

3.6.2 Surface Area by Adsorption of Water

3.6.2.1 Method

Known amounts of clay that had been dried to constant weight at 110°C were exposed to various relative humidities in closed vessels at 25.0 ± 0.2°C. The vapour pressure was determined by the nature of the saturated salt solution in each vessel. After three days the samples

were weighed daily until their weights were constant.

3.6.2.2 Results

The results for the Mangawara and Ohaupo clays are shown in Table 3.2 (each value is the mean of either two or three samples). The plots of $p/x(p_0 - p)$ against p/p_0 became curved at values of $p/p_0 > 0.35$ so that calculations could only be done with lower relative humidities.

A linear regression best fit analysis of the form $y = ax + b$ was made, using a Hewlett Packard 9100a calculator and programme 09100-70803, for the lower relative humidity measurements and the surface area was calculated from the coefficients obtained. The value of the correlation coefficient, r , is given in each case and as $r \rightarrow 1$ the linear approximation was not unreasonable.

The surface areas obtained for the two clays were 70 and 420 m^2g^{-1} for the Mangawara and Ohaupo clays respectively. The value for the allophane whole clay fraction is in excess of that obtained by Milestone¹¹ for just the fine clay part of the same material. Although the surface area found here lies within the range of other determinations for allophane by the adsorption of water^{11, 23, 24} the discrepancy noted above suggested an alternate adsorbate should also be used. To allow comparison with published data the adsorption of nitrogen gas at its atmospheric boiling point was chosen.

3.6.3 Surface Area by Adsorption of Nitrogen

3.6.3.1 Method

The sorption of nitrogen gas by various clay samples was determined at 77.4 K using a BET apparatus similar to that described by Salzburg *et al.*⁵⁴ The sample was degassed at 120°C and 0.1 Pa prior to adsorption for which the method described by Salzburg *et al.* was followed.

Table 3.2 Surface Area by Water AdsorptionOhaupo (< 2 μm)

p/p_o	% weight increase	moles H_2O per g clay	$\frac{p}{x(p_o - p)}$
0.083	4.14	2.3×10^{-3}	38.9
0.113	5.95	3.3×10^{-3}	38.5
0.327	12.2	6.8×10^{-3}	72
0.53	16.2	9.0×10^{-3}	126
0.75	23.3	1.29×10^{-2}	230
0.86	28.2	1.57×10^{-2}	392

for $p/p_o < 0.35$ $\frac{p}{x(p_o - p)} = 142 p/p_o + 25, (r = 0.992)$

Surface Area = $\underline{420 \text{m}^2 \text{g}^{-1}}$

Mangawara (< 2 μm)

p/p_o	% weight increase	moles H_2O per g clay	$\frac{p}{x(p_o - p)}$
0.083	1.03	5.70×10^{-4}	157
0.113	1.37	7.57×10^{-4}	167
0.327	2.50	1.39×10^{-3}	342
0.53	3.40	1.89×10^{-3}	597
0.75	6.47	3.60×10^{-3}	832
0.86	9.80	5.45×10^{-3}	1120

for $p/p_o < 0.35$ $\frac{p}{x(p_o - p)} = 812 p/p_o + 84, (r = 0.998)$

Surface area = $\underline{70 \text{m}^2 \text{g}^{-1}}$

3.6.3.2 Results

The results of the experiments are shown in Table 3.3. Again a regression analysis was made, this time over all pressures, and the value of the correlation coefficient, $r \rightarrow 1$, indicated that a good fit was obtained. The Mangawara halloysite had a similar surface area to that determined by the adsorption of water; viz., 78 versus 70 m^2g^{-1} , which is somewhat lower than that of allophane but it is consistent with the degree of crystallinity enjoyed by halloysite and also the very fine particle size of this sample. The surface area of the Ohaupo allophane measured with nitrogen was significantly lower than its area by water adsorption; viz., 250 against 420 m^2g^{-1} . The surface area determined for the Tirau allophane agreed well with the figure reported by Birrell and Fieldes;⁴⁵ these were 320 and 330 m^2g^{-1} respectively.

3.6.4 Discussion

The surface areas reported for a number of clay minerals, determined by using different adsorbates, are given in Table 3.4. The different methods tend to be consistent except for determinations made with water and glycerol on montmorillonite and allophane.

Montmorillonite is a layer mineral which has negatively charged aluminosilicate sheets held together by cations. Water and other small polar molecules may diffuse in between the sheets, causing expansion of the mineral, until a monolayer is built up.⁵⁵ This interlamellar diffusion is not available to non-polar nitrogen and so it is able to condense only under the external surfaces.

As much of the surface of allophane is internal and found within pores and interstices this material will have a greater capacity to adsorb small molecules able to pass through narrow passages. If the adsorbent gas is also polar and capable of swelling layer minerals it would be likely to penetrate further into crevices. Thus a monolayer of water molecules would cover a greater surface area than would a

Table 3.3 Surface Area by Adsorption of Nitrogen

Ohaupo (< 2 μm , 0.281 g)

p/p_o	moles N_2 adsorbed, (x)	$\frac{p}{x(p_o - p)}$
2.04×10^{-2}	6.22×10^{-4}	33.5
3.16×10^{-2}	6.50×10^{-4}	50.2
4.25×10^{-2}	6.75×10^{-4}	65.8
5.09×10^{-2}	7.01×10^{-4}	76.6
5.95×10^{-2}	7.14×10^{-4}	88.5
6.74×10^{-2}	7.27×10^{-4}	99.3

$$\frac{p}{x(p_o - p)} = 1392 \, p/p_o + 5.8 \quad (r = 0.9998)$$

$$\text{Surface area} = \underline{250 \, \text{m}^2\text{g}^{-1}}$$

Mangawara (< 2 μm , 0.454 g)

p/p_o	moles N_2 adsorbed, (x)	$\frac{p}{x(p_o - p)}$
5.07×10^{-2}	3.72×10^{-4}	143
8.66×10^{-2}	3.93×10^{-4}	242
1.29×10^{-1}	4.10×10^{-4}	359
1.69×10^{-1}	4.48×10^{-4}	453
2.12×10^{-1}	4.60×10^{-4}	585
2.53×10^{-1}	4.84×10^{-4}	699

$$\frac{p}{x(p_o - p)} = 2734 \, p/p_o + 3.2 \quad (r = 0.9996)$$

$$\text{Surface area} = \underline{78 \, \text{m}^2\text{g}^{-1}}$$

Tirau (< 2 μm , 0.173 g)

p/p_o	moles N_2 adsorbed, (x)	$\frac{p}{x(p_o - p)}$
4.89×10^{-2}	6.02×10^{-4}	85.5
8.2×10^{-2}	6.27×10^{-4}	143
1.17×10^{-1}	6.61×10^{-4}	201
1.88×10^{-1}	7.10×10^{-4}	326
2.24×10^{-1}	7.29×10^{-4}	395

$$\frac{p}{x(p_o - p)} = 1760 \, p/p_o - 2.2 \quad (r = 9998)$$

$$\text{Surface area} = \underline{320 \, \text{m}^2\text{g}^{-1}}$$

Table 3.4 Surface Areas of some Clay Minerals

Material	Surface Area and Adsorbate (m ² g ⁻¹)			Ref.
	nitrogen	water	glycerol	
Kaolinite	15.5		30	56
" W. Aust.	36	29		23
" Rotorua	40	9		23
Halloysite (7Å)	43			56
" (10Å)	50	19		23
Montmorillonite	27-40	400-440		55
"			460-480	57
"	47	300		23
Allophane, Egmont	138	495		23
" Whenuapai	172			22
" Tirau	330			45
" "	320			*
" Whakamaru		855		58
" Ohaupo (fine)		350		11
" various Ando	130	500		24
" Ohaupo (< 2 μm)	250	420		*

* This study.

monolayer of larger nitrogen molecules.

A disadvantage with using water as the adsorbate for surface area determinations of allophane is that it is a major component of the mineral. Before adsorption the surface water must be removed but the amount lost during drying is dependent upon the treatment,²² particularly the dehydrating temperature and the time allowed. (Water is lost by allophane from room temperature to about 300°C which gives it an endothermic peak in its DTA curve;⁴⁵ see section 3.12.) Some of this water is an integral part of the structure and may be replaced from atmosphere in a manner other than surface monolayer formation. Quirk⁵⁹ has pointed out that water tends to congregate about cation sites in non-monolayer manners; this was also observed by Kutilek⁶⁰ particularly with acid-form clays. Birrell⁶¹ also found an increased surface area for allophane when determined with water. His preparation, like that employed here, would not necessarily have removed all free cations and so clusters of water may have been present about these centres and given an enhanced capacity and apparent surface area.

The surface areas determined here correspond well with published values. The surface areas that will be used in subsequent discussions in this thesis will be those from nitrogen adsorption.

3.7 Particle Size Studies

3.7.1 Introduction

By far the greatest surface area, and hence the reactivity, of the inorganic part of a soil towards microscopic, molecular and ionic species is associated with the fine particle fractions, i.e., the clays. The large particles contribute much bulk but little reactivity; their presence also prevents the formation of suspensions of constant composition because of their rapid rate of sedimentation. For these reasons it is desirable to separate the clay fraction from the remainder

and this is most commonly done by sedimentation and centrifugation. A comparison of the surface area and the distribution of particle size allows some comment upon the nature of the active clay body to be made. This distribution will effect the colloid properties of the material, in particular its suspension stability, flocculation and coagulation with other colloids.

Particle size distributions may be made by optical methods, electron microscopy or from sedimentation and centrifugation. The large number proportion of very fine particles in relation to the contribution they make to the total mass of allophane makes the optical methods of dubious value. In the absence of suitable electron microscopy facilities at the stage when this study was made, a method based upon centrifugation was developed. In this section the theoretical basis for particle separation by sedimentation and centrifugation will be presented and then extended for particle size distribution determination.

3.7.2 Differentiation and Separation

Size differentiation of colloidal particles can be made because of the differences in the rates at which they can pass through a fluid medium which resists their movement when they are being operated upon by a mass related force. This process is idealised by Stokes's Law which states that the frictional resistance, F_r , offered a perfect sphere moving through a fluid under a condition of streamline (viscous) flow is;

$$F_r = 3\pi D\eta \cdot \frac{dx}{dt} \quad (3.5)$$

where D is the particle diameter, η is the fluid viscosity and dx/dt is the velocity. Movement by a mass related force, F_a , gives;

$$F_a = m \cdot \frac{d^2x}{dt^2} \quad (3.6)$$

$$= \frac{\pi}{6} D^3 \Delta\rho \cdot \frac{d^2x}{dt^2} \quad (3.7)$$

where m is the particle mass, d^2x/dt^2 is the acceleration induced and $\Delta\rho$ is the difference between the densities of the particle and the fluid. At the terminal velocity;

$$F_r = F_a$$

$$\therefore \frac{\pi}{6} D^3 \Delta\rho \frac{d^2x}{dt^2} = 3\pi D\eta \cdot \frac{dx}{dt} \quad (3.8)$$

When the force acting upon the colloid is gravity d^2x/dt^2 can be replaced by g , the gravitational acceleration constant. Substitution of colloid parameters in (3.7) shows that the terminal velocity, v_t , of the particle under gravity is reached rapidly and this rate can be calculated for any specific particle;

$$v_t = \frac{dx}{dt} = \frac{D^2 \Delta\rho g}{18\eta} \quad (3.9)$$

Knowledge of v_t allows predictions of the time required for all particles with diameters greater than a desired size to sediment a given distance. When particles become too small Brownian motion impedes sedimentation and the times required become excessive. For clays this limit is reached at about 1 μm . Smaller particles need larger forces such as those available in the centrifuge.

Under centrifugation the acceleration at a distance r from the axis is given by;

$$\frac{d^2r}{dt^2} = \omega^2 r \quad (3.10)$$

where ω is the centrifuge angular velocity (in radians per second).

(3.7) now becomes

$$\frac{\pi}{6} D \Delta\rho \omega^2 r = 3\pi\eta D \cdot \frac{dr}{dt} \quad (3.11)$$

Once again the terminal velocity is attained rapidly but it is now

dependent upon the distance of the particle from the axis;

$$\frac{dr}{r} = \frac{D^2 \Delta \rho \omega^2}{18\eta} dt \quad (3.12)$$

Integration of (3.11) over the maximum distance a particle may travel in time t yields;

$$\ln \frac{R}{S} = \frac{D^2 \Delta \rho \omega^2}{18\eta} t \quad (3.13)$$

R is the distance from the collecting plane to the axis and S is the radius to which the centrifuge is filled.

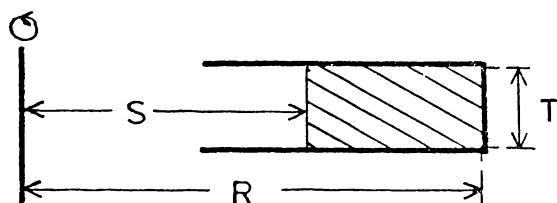


Figure 3.1 Parameters of the centrifuge.

It must be noted that the theories discussed have been developed for spherical particles. Most colloids are not spherical but they can be differentiated according to their behaviour under strong forces. The value of D is then the equivalent spherical diameter, (esd); i.e., the diameter of the sphere of the same density to which the colloids behaviour is analogous. Convenient nomographs of sedimentation times plotted against particle diameter (esd) for gravity and centrifugal sedimentation have been prepared by Tanner and Jackson.⁶²

3.7.3 Method Used for Size Fraction Differentiation

Particle sizes greater than $2 \mu m$ esd were separated from dispersed soils by repetitive sedimentation for times determined using (3.8). The suspended clays ($< 2 \mu m$) were combined and if desired smaller size fractions were separated by repetitive centrifugation under conditions determined using (3.12). Usually five or six repeated cycles were

required. These were carried out in an MSE Multex centrifuge at room temperature.

3.7.4 Size Distribution

Determination of the particle size distribution can be achieved by exhaustive repetitive centrifugation for defined size fractions. This approach is tedious and laborious for more than a few fractions.

Murley⁶³ described a method which allows a continuous distribution determination to be carried out readily by centrifugation. (3.12) shows that the diameter of a sedimented particle is dependent upon the time of running, the centrifuge speed, the collecting plane radius, R , and the inner liquid radius S . A convenient method involves variation of only S and weighing either the amount of precipitate or determining the amount of material still in suspension. This method was described for use in a disc centrifuge⁶³ but as this type of apparatus was not available the theory was modified for use with a bucket centrifuge with cylindrical tubes. A source of error was introduced because the conditions did not change instantaneously at the ends of the process as presupposed; this was reduced to some extent by operating for relatively long periods. Furthermore, as particles moved along a radius away from the axis of rotation, a small proportion of them would strike the tube walls; no account of this was taken although it would not be a large problem as only small volumes of liquid were taken and so the walls would lie in the path of only a few particles.

If the inner radius of the centrifuging system is decreased by a small amount dS the extra weight of sample in the tube is given by $\frac{\pi}{4} cT^2 \cdot dS$ where c is the weight of solid per unit suspension volume and T is the tube diameter. For this extra amount only those particles with a size larger than the equivalent diameter D given by (3.12) will reach the collecting plane after time t , whilst those with a smaller diameter than D will not. The extra weight of material deposited at the

collecting plane by this change in the top surface radius will be;

$$dW = \frac{-\pi}{4} T^2 c \cdot dS \int_D^{\infty} f(D) \cdot dD \quad (3.13)$$

The negative sign arises because the extra sample must decrease S. If the suspended material is being analysed it is necessary to consider the particles with size less than D by integrating the distribution function, $f(D)$, over the range 0 to D.

$$dW = \frac{-\pi}{4} T^2 c \cdot dS \int_0^D f(D) \cdot dD \quad (3.14)$$

As $f(D)$ is the distribution function then $\int_a^b f(D) \cdot dD$ will be the cumulative weight proportion in the range a to b. (Thus in an experiment variation of only S is enough to determine the cumulative weight percentage and hence the proportion of the sample any fraction represents.) The tangent to the curve of a plot of S against W yields the derivative dS/dW for that particular value of S and, from (3.12), a unique value of D, which when divided by the term $\pi T^2 c/4$ gives the cumulative weight fraction up to that value.

$$\int_D^{\infty} f(D) \cdot dD = \frac{-4}{\pi T^2 c} \cdot \frac{dW}{dS} \quad (3.15)$$

If a volume x of suspension is added to the centrifuge tube then;

$$S = R - \frac{4x}{\pi T^2} \quad (3.16)$$

W can be plotted against x and so the derivative dW/dx can be found. In addition

$$\frac{dW}{dS} = \frac{dW}{dx} \cdot \frac{dx}{dS} \quad (3.17)$$

$$= \frac{dW}{dx} \cdot \frac{-\pi T^2}{4} \quad (3.18)$$

$$= -\frac{\pi}{4} T^2 c \cdot \int_D^{\infty} f(D) \cdot dD \quad (3.19)$$

$$\therefore \int_{D'}^{\infty} f(D) \cdot dD = \frac{1}{c} \frac{dW}{dx} \quad (3.20)$$

W can be expressed as a function of x by determination of a degree n least squares fit polynomial of the type

$$W = \sum_1^n a_n x^n \quad (3.21)$$

$$\therefore \frac{dW}{dx} = \sum_1^n n \cdot a_n x^{n-1} \quad (3.22)$$

$$\therefore \int_D^{\infty} f(D) \cdot dD = \frac{1}{c} \sum_1^n n \cdot a_n x^{n-1} \quad (3.23)$$

The esd can be calculated from (3.12) and (3.16);

$$D = \left[\frac{18\eta}{\Delta\rho\omega^2 t} \cdot \ln \left(\frac{R}{R - \frac{4}{\pi T^2 x}} \right) \right]^{\frac{1}{2}} \quad (3.24)$$

This finally allows a plot of the cumulative distribution function against particle size.

Furthermore, the proportion of the material in the size range D_1 to D_2 is given by;

$$\int_{D_2}^{D_1} f(D) \cdot dD = \int_{D_1}^{\infty} f(D) \cdot dD - \int_{D_2}^{\infty} f(D) \cdot dD \quad (3.25)$$

$$= \frac{1}{c} \left\{ \sum_1^n n a_n x_1^{n-1} - \sum_1^n n a_n x_2^{n-1} \right\} \quad (3.26)$$

where x_1 and x_2 can be found for D_1 and D_2 respectively using (3.24).

Two further distributions of interest are the number and surface area distributions, i.e., the number of particles of esd D and their surface area assuming that they are spheres. If dW is the mass of particles of esd D then the actual number of particles this is N, given by;

$$N = \frac{6}{\pi\rho D^3} \int_D^{D+dD} f(D) \cdot dD \quad (3.27)$$

The surface area for the same mass, A_o , is given by;

$$A_o = \frac{6}{\rho D} \int_D^{D+dD} f(D) \cdot dD \quad (3.28)$$

For comparison between samples it is necessary to normalise these parameters with respect to some property and this can be done for the mass by dividing by the cumulative weight for the whole sample in the size fraction of interest.

3.7.5 Method used for Particle Size Distribution Analysis

Duplicate samples of stable salt-free clay suspensions, prepared by sedimentation of dispersed organic-free soil (see section 3.2) to produce particles of less than about 4 μm esd were measured into the cylindrical tubes of an International clinical centrifuge model CL. This was run for a set time at a constant speed determined with an electronic stroboscope. After stopping slowly the supernatant liquid was discarded and the precipitate was washed into glass centrifuge tubes, flocculated with one or two drops of dilute hydrochloric acid, collected by centrifuging, dried overnight at 110°C and weighed. The concentration of the original suspension was measured in a like manner.

A least squares fit 4th or 5th degree polynomial of the form of (3.21), which expressed the precipitate weight, W , as a function of the volume of suspension added, x , was obtained for each sample using a STATUS program (reproduced in Appendix I) run in an IBM 1130 computer. Plots of these functions were superimposed upon the experimentally determined values with the aid of a Hewlett-Packard Model 9100A calculator-plotter. This instrument was also used to plot the cumulative distribution function (3.23) against the particle diameter (esd) from (3.24). A PDP-11/05 computer was used to calculate values for the weight, number and surface area distribution functions with respect to the diameter and also to calculate the cumulative values for the weight

and surface areas of some fractions.

3.7.6 Results

Figure 3.2 shows the weight of sediment collected against the volume of suspension taken for the three clays. The curve superimposed upon these points is the best fit polynomial, in each case found to be of the 4th degree, i.e., $W = \sum_{n=1}^4 a_n x^n$. (If $n \leq 0$ the polynomial would not pass through the origin so that a necessary condition was $n > 0$.) The coefficients for the various polynomials are given in Table 3.5.

Table 3.5 Coefficients of the Least Squares Fit Polynomial (3.21) for Ohaupo, Mangawara and Tirau Clays

Clay	Coefficients			
	first	second	third	fourth
Ohaupo	3.30310	-0.11388	0.00369	-0.00005
Tirau	1.70707	-0.02821	-0.00138	0.00005
Mangawara	9.68507	-0.86445	0.04786	-0.00094

In figure 3.3 the distribution function, $f(D)$, has been plotted against the equivalent spherical diameter, D . The percentage by weight of the total material of diameter less than D is given by the area beneath the curve from 0 and D . All three clays were quite distinct. The Mangawara halloysite had only a small proportion greater than $1 \mu\text{m}$ and whilst more than 50% of its mass was associated with particles smaller than $0.5 \mu\text{m}$. The Ohaupo allophane was somewhat coarser with more material larger than $1 \mu\text{m}$ and less very fine material; its mean diameter on a weight basis was $0.7 \mu\text{m}$. The Tirau allophane was even coarser with a mean diameter of $1 \mu\text{m}$ and very little fine material. The sharp cut-off above $1.5 \mu\text{m}$ may be due to a loss of this fraction in preparation. About 5% of this clay was very fine, i.e., less than

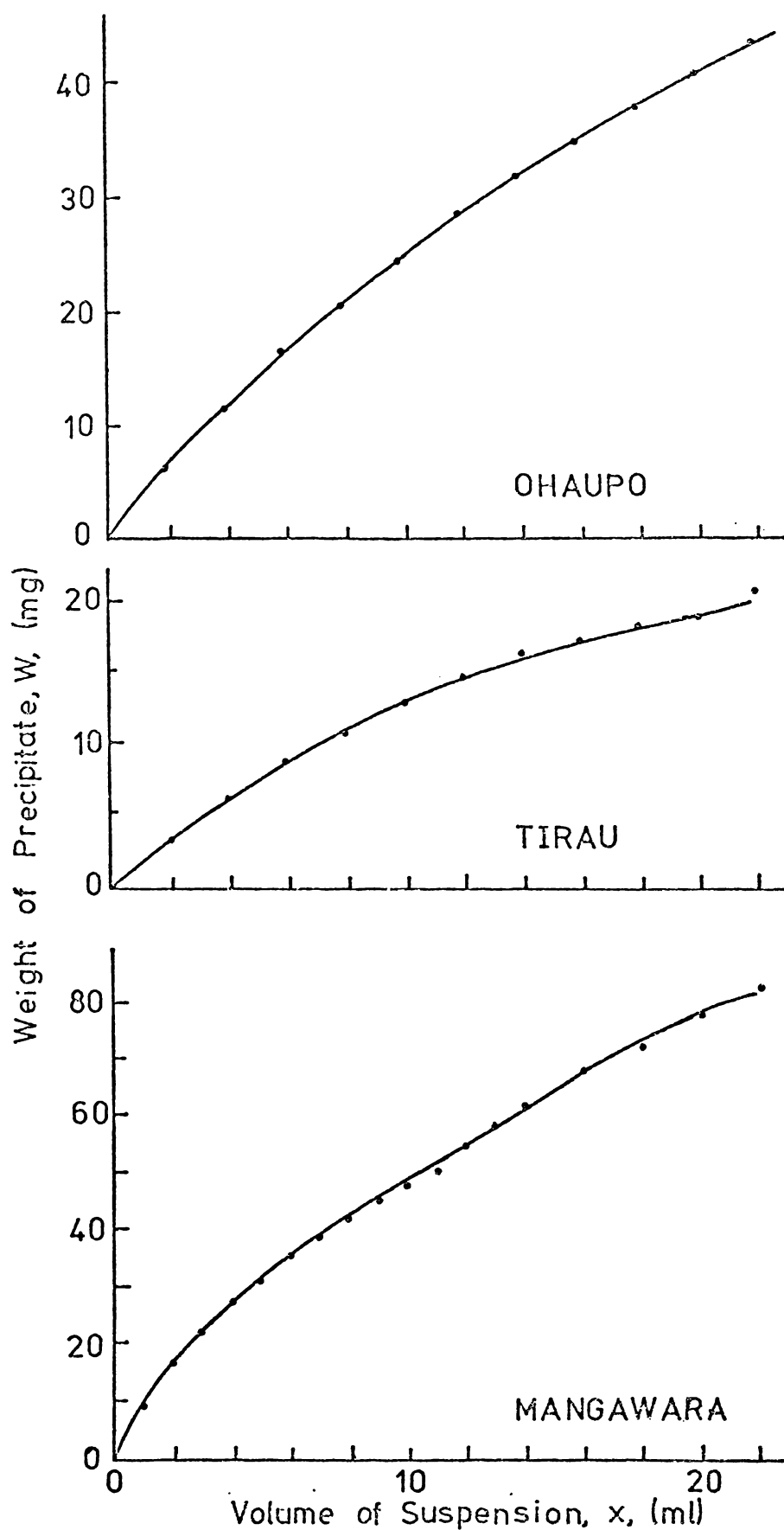


Figure 3.2. Weight of sediment collected by centrifugation from some clay suspensions. The best-fit polynomial has been superimposed over the experimentally determined values.

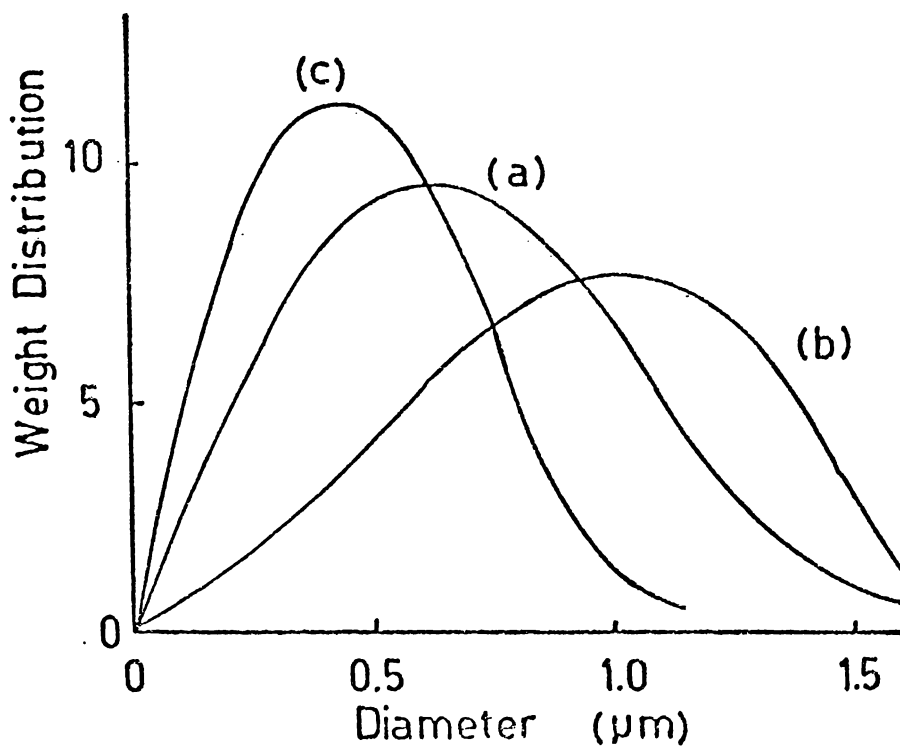


Figure 3.3. Weight-estd distributions. (a) Ohaupo (b) Tirau (c) Mangawara.

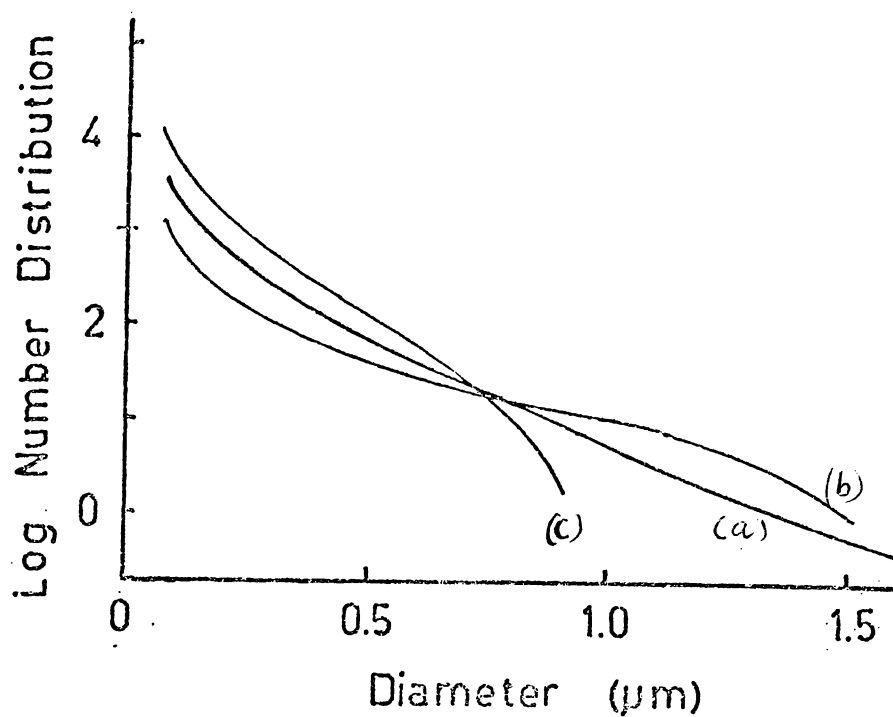


Figure 3.4. Particle number-estd distributions. (a) Ohaupo (b) Tirau (c) Mangawara

0.2 μm .

Plots of the normalised number distribution are shown in figure 3.4. (Note that the ordinate is logarithmic.) The form of this distribution does not lend itself to prediction of values at small diameters and no real confidence should be placed in the actual estimates of the numbers of fine particles ($< 0.2 \mu\text{m}$) although it is clear that they are very important in the halloysite; they are of less consequence in the allophanes.

The final figure of this section, figure 3.5, shows that if the particles are all considered as solid spheres the surface area would be primarily that of the small particles of the halloysite and to a lesser extent of the Ohaupo allophane, but it would be evenly spread throughout the fraction 0 to $1.2 \mu\text{m}$ of the Tirau allophane. The surface areas based upon these calculations are:

Ohaupo allophane	$9.8 \text{ m}^2\text{g}^{-1}$
Tirau allophane	$7.3 \text{ m}^2\text{g}^{-1}$
Mangawara halloysite	$9.7 \text{ m}^2\text{g}^{-1}$

3.7.7 Discussion

The size distribution of the Tirau clay obtained here is in reasonable agreement with other reports of size distributions of clays extracted from the same soil. Fieldes and Furkert⁶⁴ reported that 2% of the clay was fine ($< 0.2 \mu\text{m}$) compared to the 5% found here. Their method of analysis was not reported. Using a Coulter Counter (which was unable to detect small particles) Cooper³⁶ found a similar wide distribution but with a mean diameter of about $1.4 \mu\text{m}$.

The variation in the particle size distribution of the three clays may be correlated with other properties. These include the age of the material, the nature of the readily soluble fraction of the aluminium associated with the clay (see section 8.3.1) and the surface area as

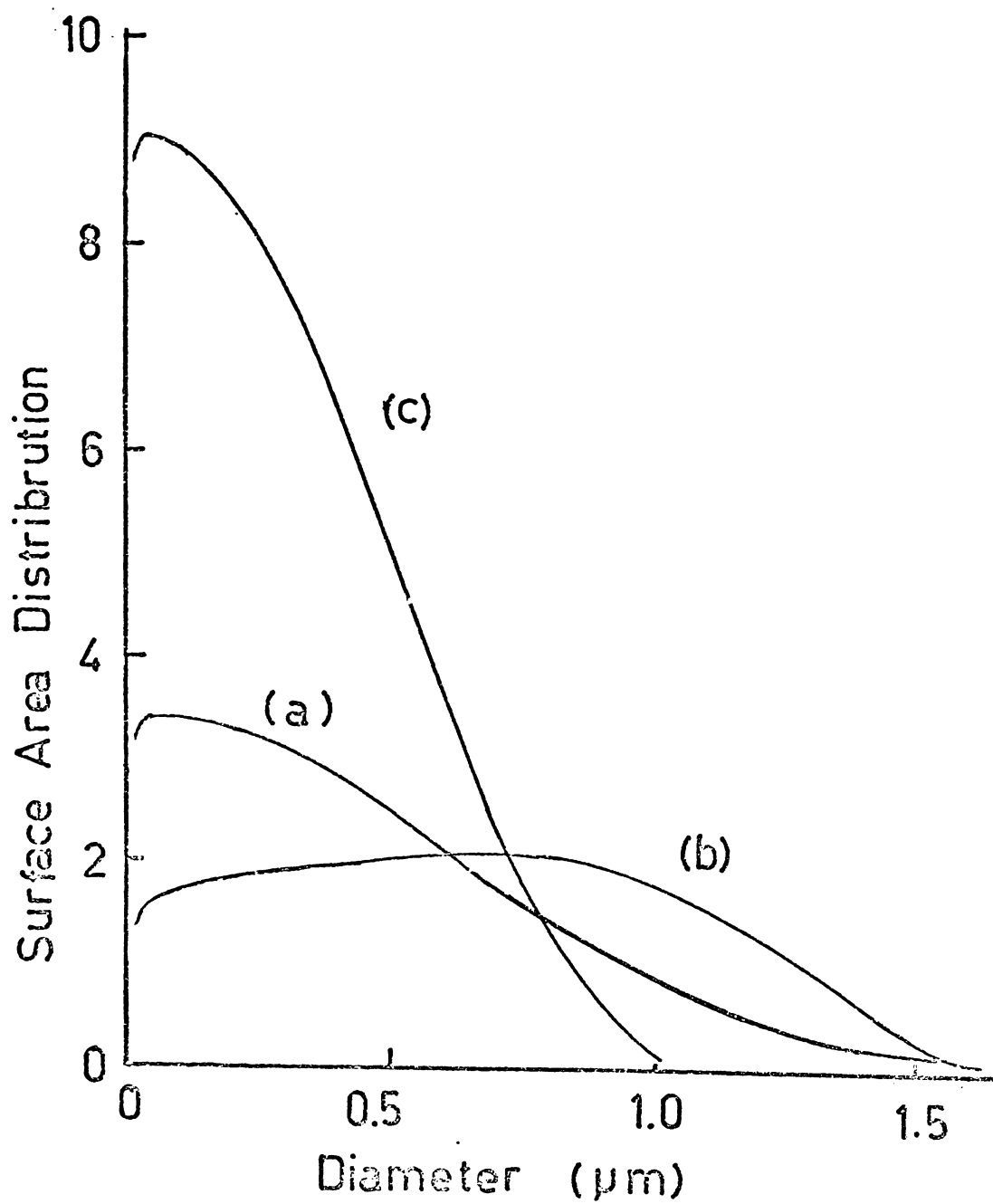


Figure 3.5. Surface area-esd distributions. (a) Ohaupo, (b) Tirau, (c) Mangawara.

determined by the adsorption of nitrogen.

The halloysite used in this work was at least a half million years old, its readily soluble aluminium was bound to species other than an infinite matrix of aluminium hydroxide and it did not have a very large surface area; $78 \text{ m}^2\text{g}^{-1}$. This is in agreement with the particle size; spheres of density the same as this clay and diameter $0.1 \mu\text{m}$ would have a specific surface area of $23 \text{ m}^2\text{g}^{-1}$ although the area calculated from the distribution was even less. The contribution from surface irregularities, from aggregates and non-spherical bodies would enhance this value somewhat. The electron micrographs, (section 3.4), Plates VII and VIII, also showed that the material was predominantly small bodies of about $0.1 \mu\text{m}$ diameter with aggregates and larger particles also present.

The Ohaupo allophane is somewhat older than the Tirau sample but much younger than the halloysite. The lability of its aluminium and its surface area were both intermediate between the other two clays. Because the mean particle size was larger, as confirmed by the electron microscope, Plates III to VI, it would be expected to have a lower surface area than the halloysite. However, its specific surface area was much greater; viz., $250 \text{ m}^2\text{g}^{-1}$. The Tirau allophane, the youngest clay studied (30,000 years), was predicted on the basis of its particle size distribution to have the lowest surface area, but in fact it had the largest, viz., $330 \text{ m}^2\text{g}^{-1}$. It also had the most labile aluminium. These facts can be reconciled if the allophane particles are considered to be aggregates of very small units, perhaps as small as 5 nm, cemented together into large porous units by the hydrous oxides of iron and aluminium, (see section 2.4). The younger clays would be less well ordered and leached than the older clays and so they would have more surface irregularities and pores. Thus they have not only freer aluminium but as a result greater amounts of included water and hence

a lower density.

It is predicted that if the surface properties of the three clays were equivalent the Tirau allophane would be the best adsorbent because it has the largest surface area. However, because there are relatively few particles it would be a poor flocculant. On the other hand the Mangawara clay would be a good flocculant because of its small particle size but it would make only a moderately good adsorbent. The Ohaupo clay would have intermediate properties again.

3.8 Dissolution by Sodium Hydroxide

3.8.1 Introduction

Amorphous silica, alumina and aluminosilicate gels can be removed from crystalline clay materials by selective dissolution using alkaline reagents.^{65,66} Cold and hot 0.5 M sodium carbonate effectively dissolve not only most of the amorphous material,⁶⁶ but also significant amounts of crystalline substances.⁶⁷ Boiling 0.5 M sodium hydroxide, as suggested by Hashimoto and Jackson,⁶⁵ does not effect the crystalline materials as extensively⁶⁷ provided the time of interaction is not excessive.⁶⁸ Highly crystalline clays such as montmorillonite, irrespective of particle size, are much less susceptible to alkaline dissolution than poorly ordered kaolinite and halloysite⁶⁹ whilst amorphous materials appear to dissolve readily. The success of a method of selective dissolution depends upon using a time and a temperature which allow differentiation in the amounts of materials dissolved. According to de Villiers¹⁰ selective dissolution with sodium hydroxide using the method of Hashimoto and Jackson⁶⁸ was the most sensitive quantitative method for the determination of allophane in soils. It is this procedure that was used in this study. (In a recent paper Kitigawa has reported the reliability of various methods for the determination of allophane in mixtures of clays.⁷⁰ He found that the method used here

tended to over-estimate the quantity of allophane, particularly if halloysite was present. The most accurate procedure involved alternate dissolution, first in 8 M hydrochloric acid and then in 0.5 M sodium hydroxide for several cycles with weight determination after each. A method based upon the weight loss between 105 and 200°C was much more straightforward and nearly as reliable.)

3.8.2 Method

Aliquots of suspensions of the various clays and clay fractions, which contained less than 100 mg of clay, were taken in a large platinum crucible and an equal volume of 1.0 M sodium hydroxide added. The mixture was brought to the boil rapidly over a bunsen burner and held at that temperature for 2.5 minutes before being cooled in ice-water. The undissolved material was collected in a dried and weighed Gooch crucible, washed with 0.5 M sodium hydroxide, distilled water and then twice with 50% aqueous acetone. It was then dried to constant weight at 110°C and the quantity of dissolved material calculated. Iron (III) hydrous oxides had been removed from some suspensions with the citrate-dithionite reagent prior to sodium hydroxide reaction; the total loss of weight includes the loss by both processes.

3.8.3 Results and Discussion

The amounts of material dissolved by 0.5 M boiling sodium hydroxide are shown in Table 3.6. Each value is the mean of that obtained for two samples.

It is perhaps notable that the most soluble clay, the Tirau allophane, had the largest particle size. The amount of this clay dissolved was similar to that reported by other workers.^{11, 36, 58} It was suggested that the undissolved material might be feldspars and a small amount of unweathered volcanic glass.^{11, 58} Yet if the clay was first subjected to the dithionite-citrate process to remove free

Table 3.6 Dissolution of some Clays in Sodium Hydroxide

Clay	Fraction	Percent dissolved
Tirau	whole clay	81.0
	< 0.5 μm	85.0
	< 0.5 μm , Fe free	100*
Ohaupo	whole clay	75.8
	< 0.5 μm	81.0
	< 0.5 μm , Fe free	94.5**
Mangawara	< 0.5 μm , Fe free	77.5**

* insufficient left for analysis

** includes amount dissolved by dithionite-citrate reagent.

iron(III) species the combined amount lost to solution was greater and did not always leave sufficient for analysis. (The order of treatment of these reagents is not important.)⁷¹ As the sodium hydroxide and the dithionite-citrate treatments do not attack the crystalline clay minerals significantly, and as the iron(III) is a significant part of the mineral a better measurement of the allophane content of a soil might be made by using both procedures consecutively.

The lower quantity of the Ohaupo clay dissolved is consistent with it containing a significant proportion of more highly ordered components. Similar materials must also be present in the Mangawara clay. That the Mangawara clay can dissolve more readily than the weakly soluble halloysite reported elsewhere⁶⁵ would be a result of its very fine particle size and an amorphous component.

3.9 Iron Content

3.9.1 Introduction

The clays derived from the weathering of volcanic ash showers commonly contain up to 8% by weight of hydrous iron(III) oxides. The

removal of these oxides from crystalline clays often enhances the sensitivity of analytical procedures. A reliable method for their dissolution from aluminosilicates using sodium dithionite and sodium citrate was developed by Aguilera and Jackson⁷² and subsequently improved by the incorporation of a buffer, sodium bicarbonate.⁷³ This procedure is almost quantitative for the free hydrous oxides but it does not dissolve such materials as magnetite to any extent and so it does not give the total iron content of a soil.

A method for elemental analysis of insoluble silicates following fusion with sodium hydroxide, from which the total iron content can be determined, is described by Vogel (p.660).⁷⁴

3.9.2 Methods

The dithionite-citrate-bicarbonate procedure as described by Mehra and Jackson⁷³ was carried out using oven-dried samples of the clays in teflon tubes. Three extractions were found to be necessary.

The procedure described by Vogel (p.660)⁷⁴ was followed for the sodium hydroxide fusion of oven-dried material. Nickel crucibles were employed for the fusion and the melt was taken up in twice-distilled water and neutralised with concentrated hydrochloric acid.

The solutions obtained from both procedures were analysed for iron(III) by colourimetric determination of the iron(III) thiocyanate complex at 490 nm (Vogel, p.785).⁷⁴

3.9.3 Results and Discussion

The quantities of iron extracted by these two processes from the various soils and clays are shown in Table 3.7.

The total content of iron found here for the Tirau soil is in agreement with that determined spectrographically,¹⁸ (2.5% as Fe or 3.6% as Fe_2O_3).

The dithionite-citrate reagent can release more than 90% of the

Table 3.7 Iron Contents of Various Soils and Clays

Sample	Iron (% by weight as Fe_2O_3)	
	Total (fusion)	Free (dithionite/citrate)
Ohaupo soil	5.12	
	5.17	
Ohaupo clay	6.09	5.66
	6.13	5.67
Tirau soil	3.40	
	3.38	
Tirau clay		4.17
Mangawara soil	5.78	
	5.81	
Mangawara clay	5.12	4.79
	5.21	4.80

total iron found in materials of the type studied here. In such clays only a small amount of iron can be considered to be in unavailable forms, e.g., in minerals such as magnetite or substituted for aluminium in the aluminosilicate matrix of the allophane itself.⁷⁵

The free iron in these clays is thus probably not a major part of the skeletal matrix. It is more likely to be present as a discrete phase or perhaps as an adsorbed species. If a neutral aqueous suspension of a material like an aluminosilicate is supersaturated with a hydrolysing metal, such as aluminium or iron(III), the metal species will tend to deposit as a separate hydrous oxide phase; only a small part will be adsorbed by the aluminosilicate. In this way aluminium has been desorbed from montmorillonite and transferred to gibbsite.⁷⁶ The allophane structure proposed by Milestone¹¹ (fig. 2.1) should perhaps be on a colloidal scale and not on a molecular scale. Furthermore, since

the aluminium:iron(III) ratio is high (9 for the Tirau allophane) if the iron is colloidal the larger part of the tetrahedral core charge arising from isomorphous substitution will be balanced by the octahedral aluminium hydroxide and only a small part by the iron(III) colloid.

The influence of the dithionite-citrate reagent upon surface properties of allophane and similar materials is discussed further in Chapter Nine.

3.10 X-ray Fluorescence Analysis

3.10.1 Introduction

Tube excited fluorescence analysis (XRF) provides a simple and clean method for both qualitative and quantitative analysis for elements heavier than magnesium (although the efficiency is low for elements lighter than potassium). It is particularly suitable for elements of the first transition series. In this study XRF was used to determine whether any measurable elements (other than silicon, aluminium and iron) were present in the materials used in this investigation and, further, to see if their concentrations were sufficient to make them important constituents. This investigation was therefore qualitative and only approximately quantitative.

3.10.2 Method

Oven-dry clay samples were exposed to molybdenum X-radiation in an Ortec Model 6100 Tube Excited Fluorescence Analyser. The anode voltage was 25 Kv, the anode current was 20 μ A and a counting time of 200 s. The contents of the multichannel analyser were transferred to paper with an X-Y plotter to give intensity-energy spectra.

3.10.3 Results and Discussion

The spectra obtained are shown in figure 3.6. The ordinate is logarithmic and records the number of counts received for the particular

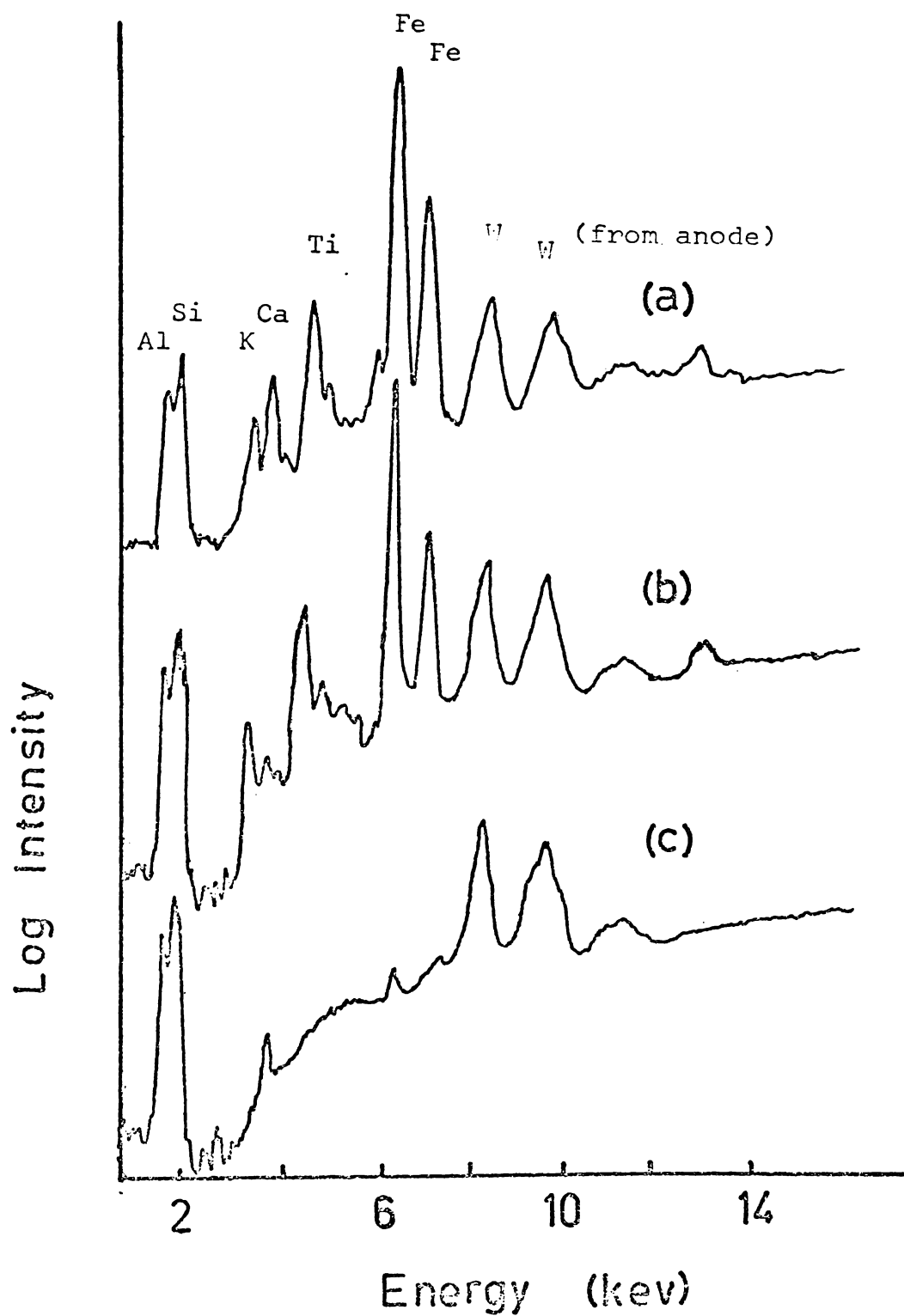


Figure 3.6. x-ray fluorescence spectra of (a) Ohaupo, (b) Mangawara clays and (c) a synthetic aluminosilicate. (Tungsten anode at 25 Kv.)

fluorescent energy. Because the efficiency of interaction with X-radiation increased with atomic number the peaks due to both silicon and aluminium are small relative to iron even though these elements were present in the clay to a greater extent. The only other element present in the Ohaupo clay in a significant quantity was titanium but its concentration would be considerably less than that of iron. Very small amounts of potassium and calcium were also present. The Mangawara clay was very similar to the Ohaupo but traces of manganese and zinc were also apparent. The elemental composition of the Tirau clay has been determined spectrographically.¹⁸ The three clays all have a roughly similar elemental composition.

The spectrum of a synthetic aluminosilicate was also determined (fig. 3.6c). Besides aluminium and silicon, and a quantity of sodium and chloride probably incorporated or adsorbed during preparation,⁷⁷ only trace amounts of calcium and iron were present.

3.11 The Optical Properties of Allophane

3.11.1 Introduction

The optical density of a suspension provides a useful method for the determination of the concentration of the colloid; it can also yield information about the size and shape of the suspended particles. Both of these features have been investigated and are commonly used for the characterisation of monodisperse sols. The visible and ultra-violet spectra of some clay minerals have been recorded to see what information they could provide about the nature of the material.⁷⁸ As the fundamental structural units of clay mineral lattices, the oxy-groups of silicon and aluminium, do not absorb light in the visible or u.v. regions (220 to 800 nm) any chromophores present will be associated with other species, notably transition metals. Although many

clays contain these elements they are usually present in trace quantities except for iron which tends to be the major contributor to the absorption spectra.⁷⁸ A study of the absorbance peaks, if they can be observed, should give some information of the nature of the metals in the chromophores of the clay.

3.11.2 Theory

The relative decrease in the intensity of light as it passed through a suspension is measured experimentally as the optical density, A , defined by Lambert's law;

$$A = \frac{1}{\ell} \log \frac{I_o}{I} \quad (3.29)$$

where I_o and I are the intensities of the incident and the transmitted light respectively and ℓ is the optical path length through the suspension. There are two components to the optical density; that due to absorption by specific atomic and molecular functions and that due to scattering caused by the differences in the refractive indices of the particle and the dispersing medium. For a narrow beam of light;

$$A = \frac{1}{\ell} \log \frac{I_o}{I_o - I_a} + \frac{1}{\ell} \log \frac{I_o}{I_o - I_s} \quad (3.30)$$

$$= 0.4343 (E + \tau), \quad (\ell = 1 \text{ cm}) \quad (3.31)$$

where I_a and I_s are the intensities of the absorbed and scattered light respectively, E is the extinction and τ the turbidity. At any specific wavelength;

$$E = \epsilon c \ell \quad (3.32)$$

where ϵ is the extinction coefficient for the absorption at that wavelength and c is the concentration of suspenoid.

The Rayleigh equation for light scattering relates the turbidity at constant wavelength to the concentration of particles, N , each of

volume V thus;

$$\tau = kNV^2 \quad (3.33)$$

where k is an optical constant. This equation holds for ideal scatterers with diameter D less than a tenth part of the wavelength, λ , but it loses validity for larger particles. If particles coalesce although the number concentration decreases the mean volume increases at a greater rate and so with the commencement of flocculation there may be an increase in the turbidity. For a flocculating system Timasheff⁷⁹ has shown that;

$$\tau = K \sum_x N_x V_x^{\frac{2}{3}} \left[\frac{V_x^{\frac{1}{3}}}{\lambda} \right]^m \quad (3.34)$$

where K is a constant, N_x is the number concentration of particles of degree of association x, $V_x = x.V$ and m is a constant which varies between 4 (for ideal Rayleigh scattering bodies) and -2 in a complicated manner and has some relation to particle size. For constant degree of aggregation, or dispersion, (3.34) can be rewritten as;

$$\tau = b \lambda^{-m} \quad (3.35)$$

and so;

$$\frac{d \log \tau}{d \log \lambda} = -m \quad (3.36)$$

The relation (3.35) has been found to hold for many dispersions (e.g., refs. 80 and 81). As the total optical density is the sum of the consumptive absorption and the turbidity, if a function which adequately describes the turbidity can be generated the difference between this function and the optical density at any wavelength will be the absorption due to the chromophores of the suspenoid.

3.11.3 Methods

Spectra of suspensions which had been washed at the centrifuge at least six times in twice-distilled water were recorded with a Cary model

17 spectrophotometer using 1 cm path length quartz cuvettes. The iron(III) colloid was prepared by refluxing a 0.1 M solution of iron(III) chloride for one hour.

Exponential curves of the form of (3.35) were superimposed upon the spectra with a Hewlett-Packard 9100A calculator-plotter.

3.11.4 Results and Discussion

The spectra for a variety of size fractions of the Ohaupo allophane are shown in figure 3.7. The exponential nature of these is evident for the smaller fractions. It is not as dominant for the larger particles particularly at lower wavelengths where the assumption that the bodies are ideal scatterers is not valid and $m > 0$ and is not constant. Figure 3.8 shows the exponential function generated by (3.35) superimposed over the spectrum of the $< 0.25 \mu\text{m}$ fraction of the clay. The spectrum deviates from ideality in that m is not a true constant but does vary with λ , again probably the result of particle diameter approaching the wavelength. The mean particle equivalent spherical diameter on a number basis is, from section 3.7.4, about $0.1 \mu\text{m}$ (100 nm); in the far uv this is only one-half the wavelength. Increasing the particle size also lessens the effect of scattering. Nevertheless, weak deviations from the exponential curves can be seen at 275, 360 and 480 nm which cannot be ascribed to variation of the exponent m but are probably associated with absorption by chromophores belonging to the colloid.

The spectra for hydrous iron(III) oxide suspension have been reproduced in figure 3.9. The superimposed curve is for the exponent $m = 4$, i.e., for an ideal scattering body. As the curve is not close to the absorbance spectrum the interaction of this colloid, unlike allophane, is dominated by consumptive absorption although scattering is still important. There are three regions of absorption and these coincide with the regions found for allophane although for the iron(III)

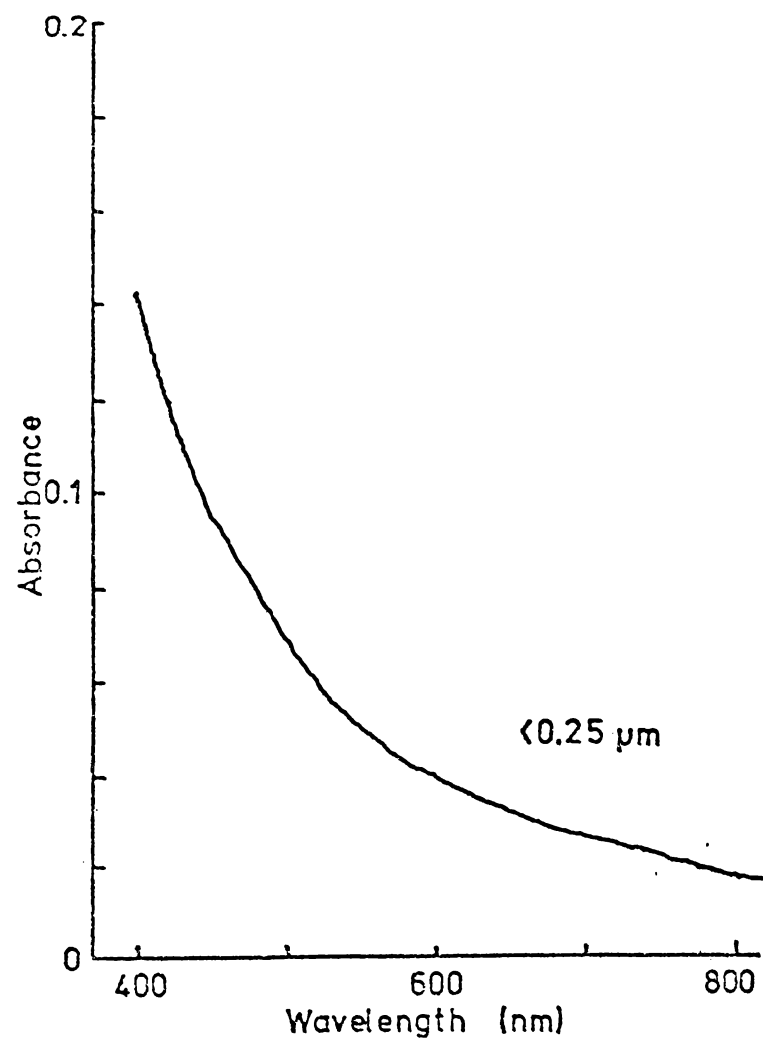
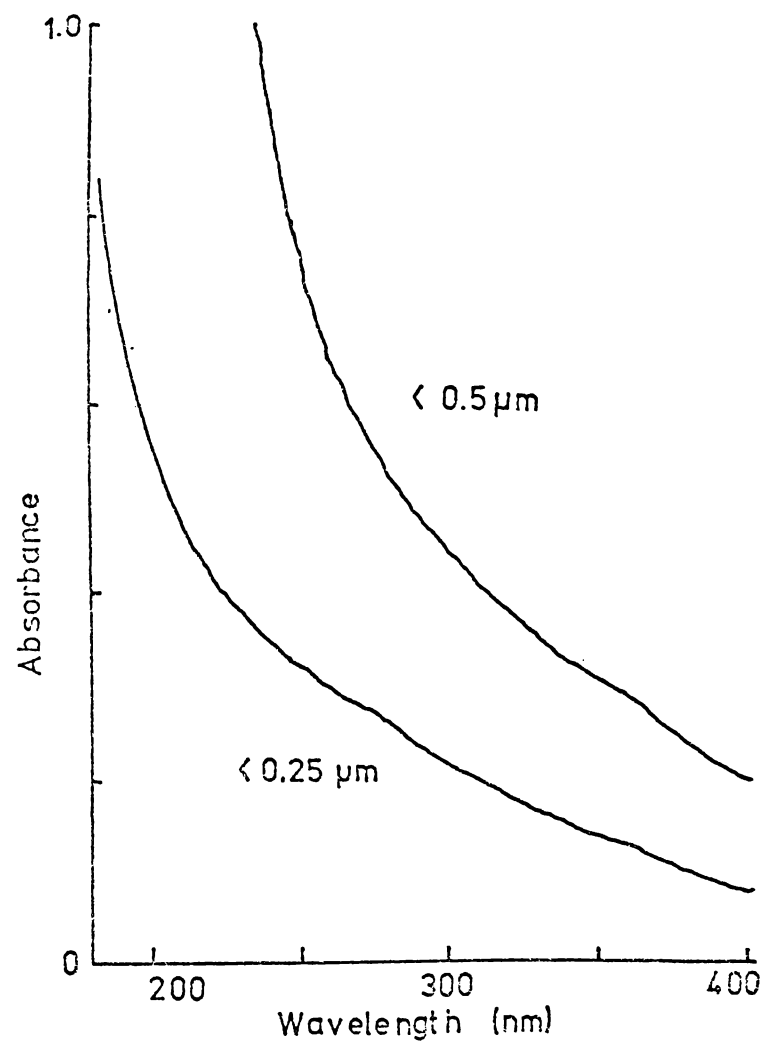


Figure 3.7. Absorbance spectra of suspensions of various fractions of Ohaupo clay.

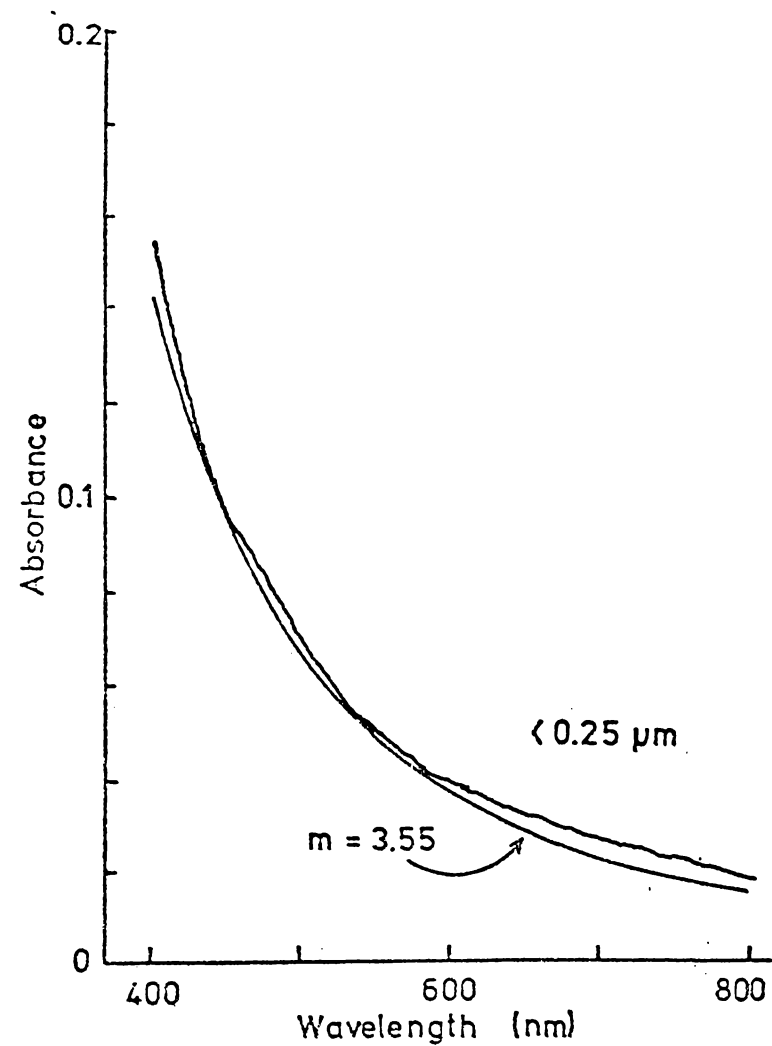
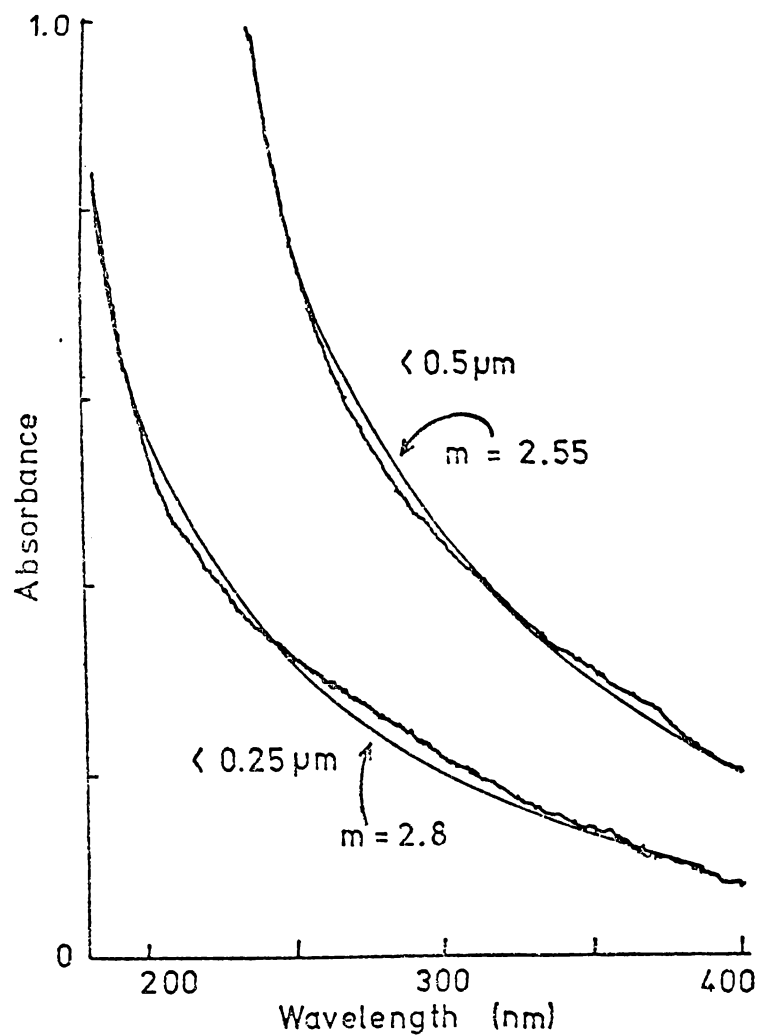


Figure 3.8. Exponential curves superimposed over absorbance spectra of various fractions of Ohaupo clay. (m is the exponent of $(3.35)^m$),

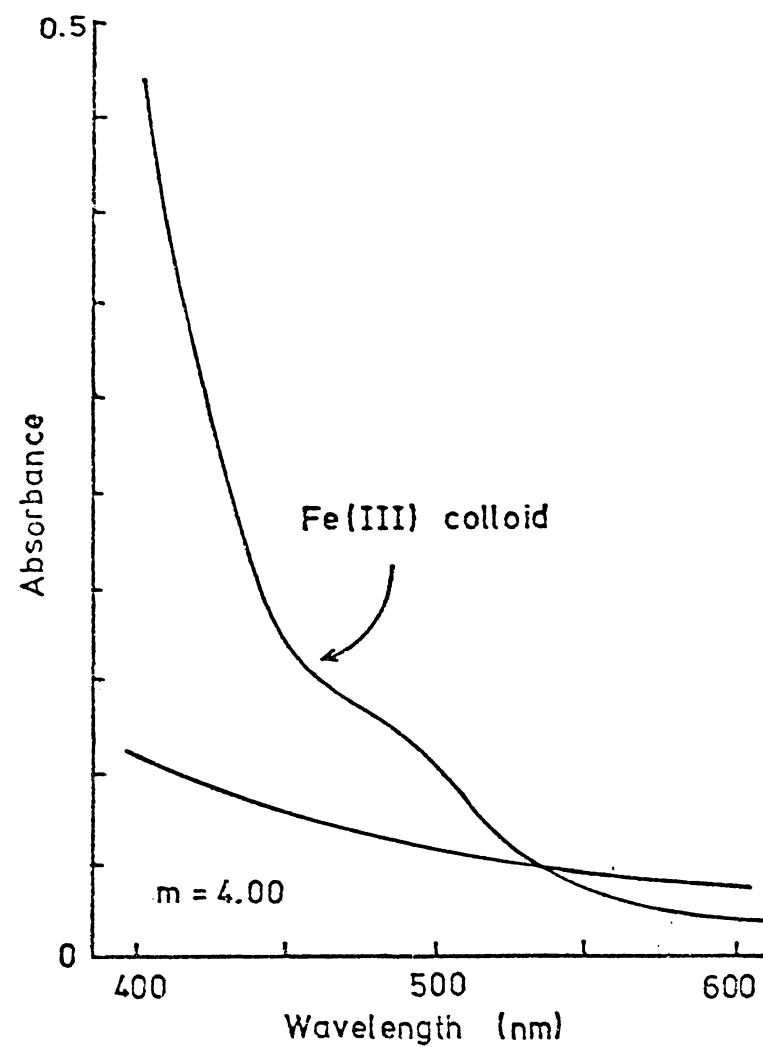
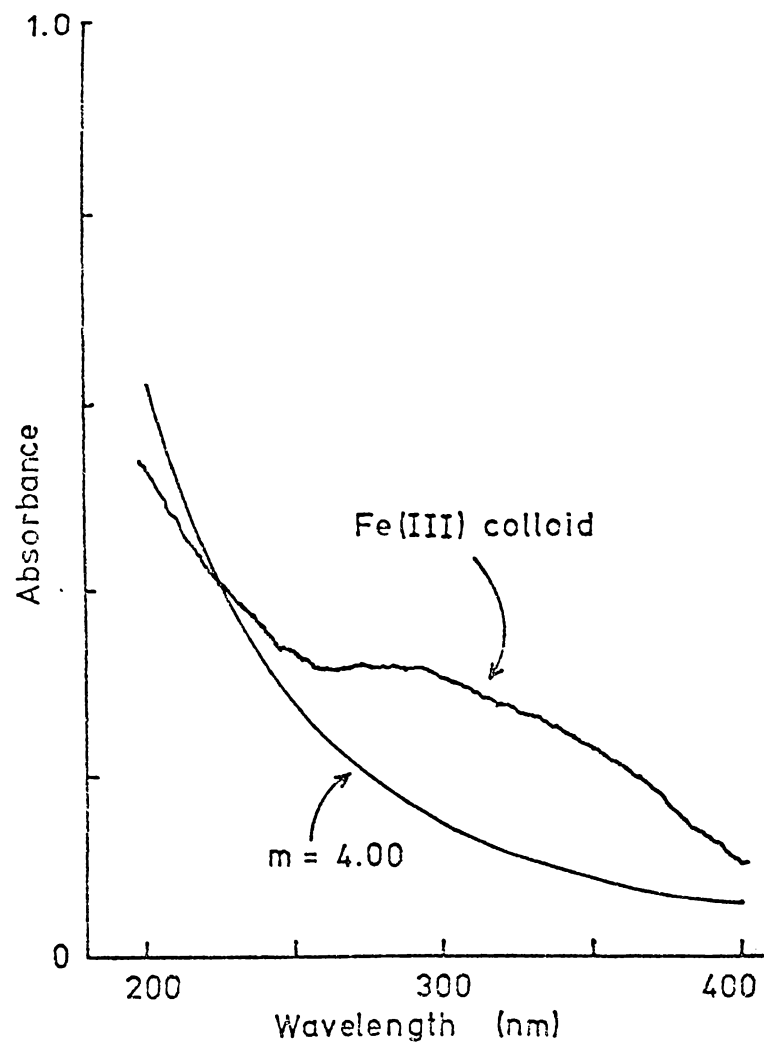


Figure 3.9. Absorbance spectra of hydrous iron(III) oxide colloid with superimposed exponential curve. (m is the exponent of (3.35)).

colloid they are considerably more intense. It would appear likely that the iron(III) found in Ohaupo allophane is in a similar state to that in hydrous iron(III) oxide.

The optical absorption spectra of a number of clay minerals have been recorded by Karickhoff and Bailey.⁷⁸ Although the clays they studied showed a roughly exponential increase in the absorbance associated with scattering a number of them gave maxima associated with transition metal absorptions. The two minerals most like allophane studied, halloysite and kaolinite, showed little absorptive absorption, and their spectra, like that of allophane, were also dominated by scattering.

3.12 Thermal Properties

Two methods of studying thermal properties of clays are commonly used. These are differential thermal analysis (DTA) and thermal gravimetric analysis (TGA). Both measure a property of the solid as it is heated.

TGA measures the weight loss with increasing temperature. Using this technique Milestone¹¹ found, for the clays extracted from a wide range of Waikato soils, that practically all weight loss was from water and occurred below 600°C, mostly between 50 and 200°C. The weight loss by freeze-dried samples of Ohaupo and Tirau allophanes was 25 and 32% respectively. This is confirmation of the expectation, based upon their densities (section 3.5), that the Tirau clay was more hydrated.

The parameter measured in DTA is the difference in temperature between the sample and a reference material as their temperature is increased at a regular rate. Heat effects associated with physical and chemical changes in the material are then recorded. These may be exothermic or endothermic and include fusion, crystal structure change, dissociation, dehydration, etc. As the temperatures at which these

occur depend upon the material, characteristic spectra can be obtained.

The DTA curves of allophane have been reported by White⁶ and also by MacKenzie.⁸² They show a large endotherm due to water loss between 60 and 350°C and an exotherm at above 1000°C from the formation of mullite. These features are generally characteristic^{29,45} and have been used as part of a definition of the mineral.⁹ Halloysite, as a member of the kaolinite group, is characterised by a sharp dehydroxylation (endothermic) just below 600°C and by an exotherm in the region 950 to 1000°C.⁸² If it is hydrated (halloysite (10Å))⁸³ there is also a large endotherm near 125°C as interlayer water escapes. Dehydrated halloysite, metahalloysite or halloysite (7Å)⁸³ show a small endothermic peak in the region 100 to 140°C.²⁹

For this study the DTA curves were determined with a Stone Differential Thermal Analyser. The spectra of the Mangawara and Ohaupo clays are presented in figure 3.10. The curve for the Ohaupo clay displays a typical allophane feature, the broad endotherm at 125°C. As the temperature did not exceed 900°C the high temperature properties could not be observed. The weak broad exotherm at 300°C and the endotherm at 470°C show that this clay also has some of the characteristics of Hamilton ash, a highly halloysite clay.²⁹ It is again evident that Ohaupo clay is a mixture of allophane and halloysite. The exotherm at 530°C in the spectrum of the glycolated sample corresponds to a halloysite content of about 17%. The curve recorded for the Mangawara clay with its endotherms at 125 and 525°C is typical of halloysite (7Å)⁸³ which contains some allophane. The peaks in between these two are obscured by the peak from the loss of glycol.

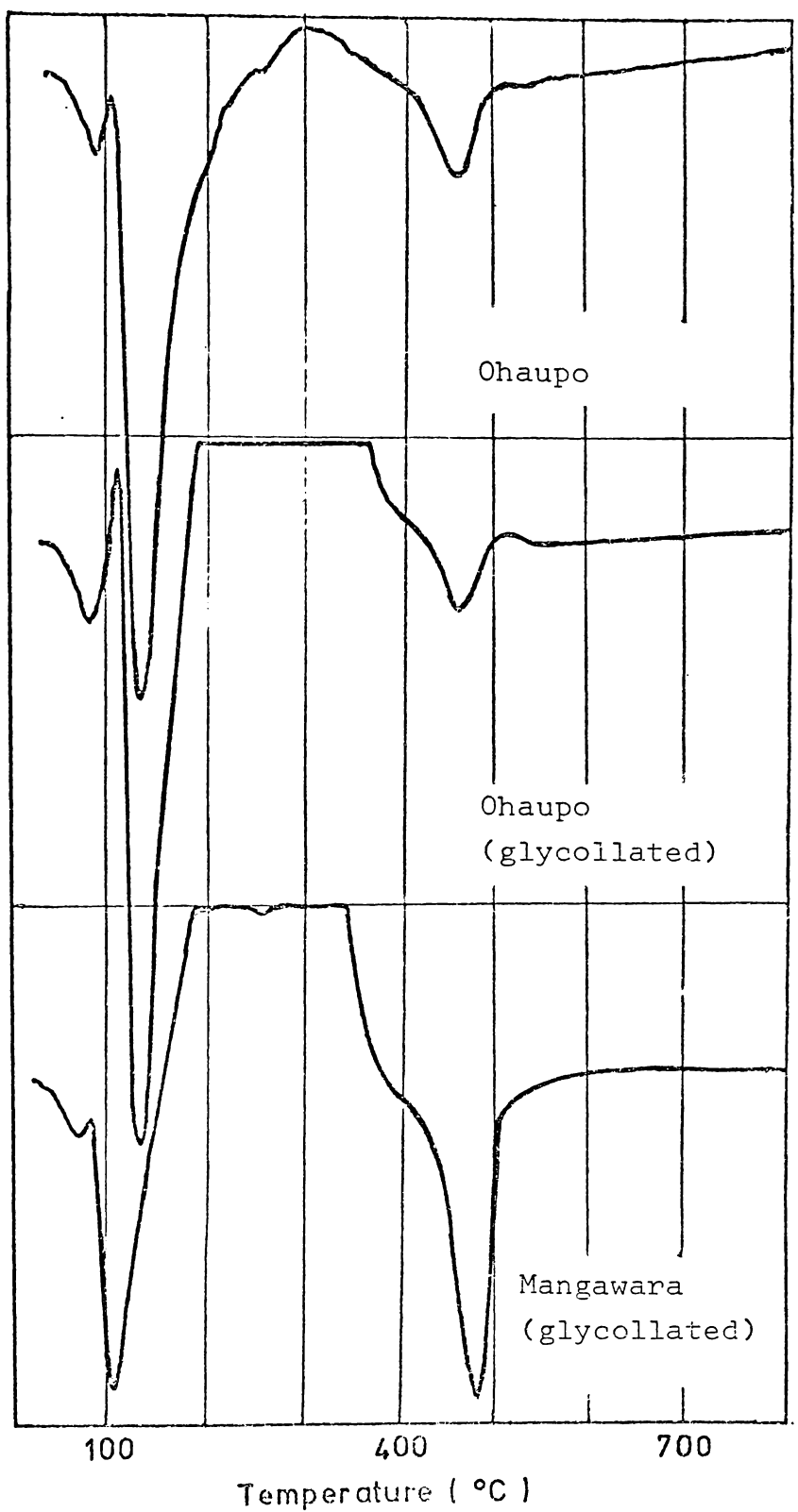


Figure 3.10. Differential thermal analysis spectra.

3.13 Conclusion

A number of physical and chemical properties of the clay fractions of soils developed on three Waikato tephra were investigated. In general standard procedures were utilised but it was found necessary to develop a centrifugal method to determine particle size distributions. A fresh approach was also used to interpret the uv-visible spectra of a clay suspension.

The three clays can now be reasonably categorised. That separated from Tirau soil was a coarse form of allophane with a high solubility in alkali and a very large internal surface area. The Ohaupo clay was predominantly allophane (about 90%) with some halloysite. It had a moderately high solubility in alkali, a high internal surface area and a high proportion of small particles. The iron(III) present in the Ohaupo clay was in a similar form to that in hydrous iron(III) oxide. Dispersion of the clay fraction from a Mangawara soil yielded a very finely divided, moderately alkali soluble halloysitic clay containing some amorphous material.

No results of this chapter have offered any evidence that would contradict the models for the allophane structure that have been proposed by Okada *et al.*²⁵ or Cloos *et al.*³⁷ (see section 2.4). The model used in further discussions will be that allophane has a tetrahedral aluminosilicate core of irregular structure and composition, coated to a variable degree with polymeric hydrous aluminium oxide. Other colloids, notably hydrous iron(III) oxides, may be adsorbed onto these units and assist the hydrous aluminium oxide in binding them into clay sized aggregates.

CHAPTER FOUR

THE ELECTROCHEMISTRY OF THE DOUBLE LAYER

4.1 Introduction

The electrochemical double layer* at the solid/liquid interface of a charged particle in a liquid medium dictates much of the behaviour of that particle, particularly its suspension, flocculation, electrokinetic and adsorption characteristics. A discussion of the double layer is made here to introduce some surface and colloid properties required in subsequent chapters of this thesis. Reference will be made to the hydrous oxides because their surface electrochemistry has been well studied, much more so than the clay minerals to which they bear many similarities. Excellent reviews of this subject include; Overbeek⁸⁴ (in Kruyt⁸⁵), Dukhin and Derjaguin,⁸⁶ Sparnaay⁸⁷ and (with particular reference to oxides) Ahmed.⁸⁸ Much relevant material can also be found in *Discussions of the Faraday Society, No.52, "Surface Chemistry of Oxides"* (1971).

In order to understand the electrokinetic and surface properties of aqueous colloids it is necessary to know the distribution of electrical charges and the potential gradients at the surface and their alterations with varying electrolytic and solution conditions. A number of concepts may appear straightforward but in many instances the real situation is less distinct, particularly with regard to the positions of adsorbed ions. One reason for this uncertainty is that the double layer is an interfacial region and the extent to which any component belongs to either bulk phase or to a third separate interfacial phase is not always determinable.

This chapter is devoted to a discussion of theories of the origin

*Electrochemical double layer is the preferred term but for brevity double layer may be used.

and nature of the distribution of charges and electrical potential at the hydrous oxide/aqueous phase interface. These theories will be used in subsequent chapters when some aspects of the electrochemical double layer at the allophane/aqueous interface will be discussed. First, however, the concept of adsorption must be dealt with.

4.2 Adsorption

When two phases are in contact although the total amount of material may be known it is impossible to determine how much belongs to each phase and to the surface itself. It becomes necessary to make an approximation and consider that the major component of each phase is not adsorbed at the interface. This will not apply to concentrated systems but these are not considered in this thesis. For dilute solutions it follows that adsorption of the minor component may occur and this will lead to a specific surface excess, Γ . This is the difference between the concentration of the adsorbing species, or adsorbate, at the surface, i.e., in a zone of depth at the surface equal at least to its diameter, and that which would occur if the surface had no influence, i.e., that of a like region in the bulk solution. A species can be considered to be adsorbed if its surface excess concentration is non-zero. If $\Gamma < 0$ negative sorption has occurred and the species has been excluded from the surface. Hereafter adsorption will be implied to be positive unless specified as negative.

4.3 Electrical Potentials at a Phase Boundary

At the interface between two different phases a potential difference frequently arises. This is because of non-equivalent effects between the interactions of the two phases with anions and cations as well as by surface group polarisation, dipole orientation,

dissociation and unequal dissolution. The potential difference over such a phase boundary, ϕ , also known as the Galvani potential, is the sum of two parts; the Volta potential, ψ , arising from the free charges, which is $1/e$ (e is the electron charge) times the work required to bring unit charge from infinity to a point close to the surface, and the surface potential, χ , arising from oriented dipoles, which is $1/e$ times the work needed to move the charge across the phase boundary into the interior. For any surface;

$$\phi = \psi + \chi \quad (4.1)$$

At an interface between two different phases this can be rewritten as;

$$\Delta\phi = \Delta\psi + \Delta\chi \quad (4.2)$$

Only the Volta potential difference, $\Delta\psi$, may be measured.⁸⁴

The total amount of work to bring the species i of charge z_i from infinity into a phase, the electrochemical potential, $\bar{\mu}_i$, is the sum of the chemical potential term and the electrostatic work term $z_i e \phi$

$$\bar{\mu}_i = \mu_i + z_i e \phi \quad (4.3)$$

$$= \mu_i^0 + kT \ln a_i + z_i e (\psi + \chi) \quad (4.4)$$

where μ_i^0 is the standard chemical potential and a_i is the activity of the species i . If i is a component of the solid matrix, i.e., it is potential determining, then variations of its concentration gives;

$$\Delta \bar{\mu}_i = \Delta \mu_i^0 + kT \Delta \ln a_i + z_i e \Delta \phi \quad (4.5)$$

But μ_i^0 cannot change and $\Delta \bar{\mu}_i = 0$ at equilibrium so that for ideal solution behaviour and assuming that χ does not change for only moderate changes of the solution composition then;

$$\Delta \psi = - \frac{kT}{z_i e} \Delta \ln a_i \quad (4.6)$$

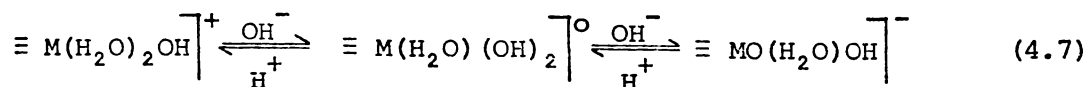
This is the Nernst equation which in this form allows approximate calculation of the surface Volta potential from the adsorption of matrix components or potential determining ions.

A surface which becomes charged by the transfer of charges across the interface in this manner forms a reversible electrochemical double layer and is found for solids such as the sparingly soluble salts and oxides. A completely polarised double layer is established when an external potential is applied across an interface. The similarity in the charge distribution in the liquid part of the double layer structure of these two systems has been shown by equilibrium studies using silver halides⁸⁵ and mercury⁸⁹ in contact with aqueous electrolytes. There is a difference between both of these materials and the hydrous oxides which will be established in Chapter Seven when cation adsorption is further considered.

4.4 Origin of the Surface Charge of the Reversible Double Layer

As has already been mentioned in the previous section an interface may become charged by non-equivalent adsorption of the potential determining (p.d.) cations and anions from solution. With a material such as silver iodide the matrix ions are of course Ag^+ and I^- so that these will be potential determining in the suspending medium. As I^- is more strongly adsorbed than Ag^+ the iodide surface tends to be negatively charged because of a surfeit of adsorbed I^- ions unless there is a large excess of the cation in the solution. The situation for hydrous oxides is a little more complex because of the solubility of the cation and its subsequent hydrolysis reactions which both depend upon the pH. This results in H^+/OH^- being the p.d. ions even though they are not the primary units of the solid. At the surface they are extremely important because of their involvement in the following reactions usually considered to be the charging mechanism of

the hydrous oxide surface;



The oxide negative charge originates from acid dissociation of hydroxyl groups and will increase with pH. This will enhance surface cation attractive interaction and induce cation adsorption to maintain electroneutrality. Sufficiently basic oxides on the other hand can be protonated by more strongly acid substances and hence acquire a positive charge which also must be balanced, this time by adsorbed anions. Amphoteric materials will display both of these properties. At some point the surface charge must equal zero and the electrolytic conditions, particularly the p.d. ion concentration, where this results is known as the point of zero charge or PZC (it has also been known as the ZPC) and for hydrous oxides it is commonly referred to by the pH of the medium at this point.

The position of the counterions or charge neutralising ions relative to the surface is of interest. Obviously they do not form part of the surface in the same manner as the p.d. ions. In the next section the distribution of ions at the solid/aqueous interface is considered in terms of some current concepts. This topic will be raised again in Chapter Seven with special reference to the nature of the relationship between adsorbed cations and the hydrous oxide surface.

4.5 Structure of the Double Layer

4.5.1 Development of Ideas

The first model for surface charge separation was proposed by Helmholtz⁹⁰ who considered the charges to be in separate planes on either side of the interface; one being negative and the other positive

i.e., a double layer. Later Perrin⁹¹ recognised that this was a molecular condensor. Since then the ionic distribution has been found to be somewhat more complex. For the effects close to the surface discussion will be restricted to planar surfaces. The implications of curved surfaces will be considered where they become important; that is, with influences of distance similar to particle size. (See section 4.8.2.)

4.5.2 The Gouy⁹² and Chapman⁹³ Diffuse Double Layer Theory

The solid phase bears a charge due to ionic or electronic excesses at its surface which is matched by an equivalent amount of charge in the solution near the surface. The surface charge is considered to be smeared out uniformly over the surface whilst the liquid phase charge is discrete and the ions which compose it are distributed to form a gradient by thermal motion.

Poisson's equation which describes the coulombic interactions of the charges in the system is;

$$\nabla^2 \psi = - \frac{4\pi\rho}{\epsilon} \quad (4.8)$$

where ∇^2 is the Laplace operator, which for a plane can be replaced by d^2/dx^2 , ψ is the potential which varies between ψ_0 at the surface and zero in the solution bulk, ρ is the charge density and ϵ the dielectric constant of the phase. The ionic distribution at any point is governed by a Boltzmann relationship which concentrates cations and repels anions in regions of negative charge, and vice versa;

$$c_i = c_s \cdot \exp\left(- z_i \cdot \frac{e\psi}{kT}\right) \quad (4.9)$$

where c_i is the concentration of ion i at a point where the potential is ψ , c_s is the concentration (in ions per unit volume) in the bulk solution, and e, k and T have their usual meanings. For any unit volume the charge density is;

$$\rho = \sum z_i e c_i \quad (4.10)$$

Combining (4.8), (4.9) and (4.10) gives;

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi}{\epsilon} \sum z_i e c_s \cdot \exp(-z_i \frac{e\psi}{kT}) \quad (4.11)$$

Multiplying both sides of (4.11) by $2d/dx$ and integrating yields;

$$\left(\frac{d\psi}{dx}\right)^2 = \frac{8\pi kT}{\epsilon} \sum c_s \left\{ \exp(-z_i \frac{e\psi}{kT}) - 1 \right\} \quad (4.12)$$

for $x \rightarrow \infty$, $\psi \rightarrow 0$ and $d\psi/dx \rightarrow 0$.

In the particular case where $z:z$ electrolytes are used or when the similion (an ion with the same charge as the surface) is unimportant because it often plays little part in the double layer from which it is repelled, then z_i may be replaced by z ;

$$\frac{d\psi}{dx} = \left[\frac{8\pi kT}{\epsilon} \right]^{\frac{1}{2}} \cdot \left\{ \exp\left(-\frac{ze}{kT} \psi\right) - \exp\left(-\frac{ze}{kT} \psi\right) \right\} \quad (4.13)$$

Electroneutrality over the double layer must apply and the surface charge, σ_o , is equalled by the charge beyond the surface;

$$\sigma_o = - \int_0^\infty \rho \, dx \quad (4.14)$$

Using (4.8) and integrating;

$$\sigma_o = - \frac{\epsilon}{4\pi} \left(\frac{d\psi}{dx} \right)_{x=0} \quad (4.15)$$

$$= \left[\frac{\epsilon kT}{2\pi} \cdot c_s \right]^{\frac{1}{2}} \cdot \left[\exp\left(\frac{ze}{2kT} \psi_o\right) - \exp\left(-\frac{ze}{2kT} \psi_o\right) \right] \quad (4.16)$$

ψ_o is the potential where $x = 0$, i.e., the surface potential.

Integration of (4.13) using $\psi = \psi_o$ when $x = 0$ produces;

$$x\kappa = \ln \frac{(E+1)(E_o-1)}{(E-1)(E_o+1)} \quad (4.17)$$

where $\kappa = \left[\frac{8\pi z^2 e^2}{\epsilon kT} c_s \right]^{\frac{1}{2}}$, $E = \exp\left(\frac{ze}{2kT} \psi\right)$, and $E_0 = \exp\left(-\frac{ze}{2kT} \psi_0\right)$.

At low potentials (4.17) can be approximated by;

$$\kappa \psi_0 = \ln \frac{\psi_0}{\psi} \quad \text{or} \quad \psi = \psi_0 \exp(-\kappa x) \quad (4.18)$$

and it can now be seen that the potential drops off by the factor $1/e$ over a distance of the order of $1/\kappa$. Under these conditions the double layer is equivalent to a capacitor of separation $1/\kappa$. This distance, $1/\kappa$, is often referred to as the double layer thickness or alternatively as the Debye length. For aqueous solutions of 1:1 electrolytes $1/\kappa = 3.06 c_s^{-\frac{1}{2}} \cdot 10^{-10}$ m.

A plot of the distribution of ions behaving according to this system is presented in figure 4.1. Although the ion concentrations are reasonable in the more diffuse parts of the interfacial region at distances in the order of less than atomic dimensions unrealistic values are predicted.

4.5.3 Stern and Grahame Modifications to the Double Layer Theory

The major discrepancies of the previous section occur within the first layers of atoms and ions close to the surface. Stern⁹⁴ considered the possibility that ions could only approach within a distance d of the surface which has a maximum capacity and that specific adsorption* of ions could also occur on this plane. It is this division of the region into two parts, the fixed layer, where ions and solvent molecules are bound to the surface, and the diffuse layer, which merges into the bulk liquid where they are free, that is of great importance in understanding the surface electrochemistry of hydrous oxides and clays.

*So-called specific adsorption includes adsorption influenced by effects other than just pure coulombic attraction. In particular it means some covalent bond formation occurs.

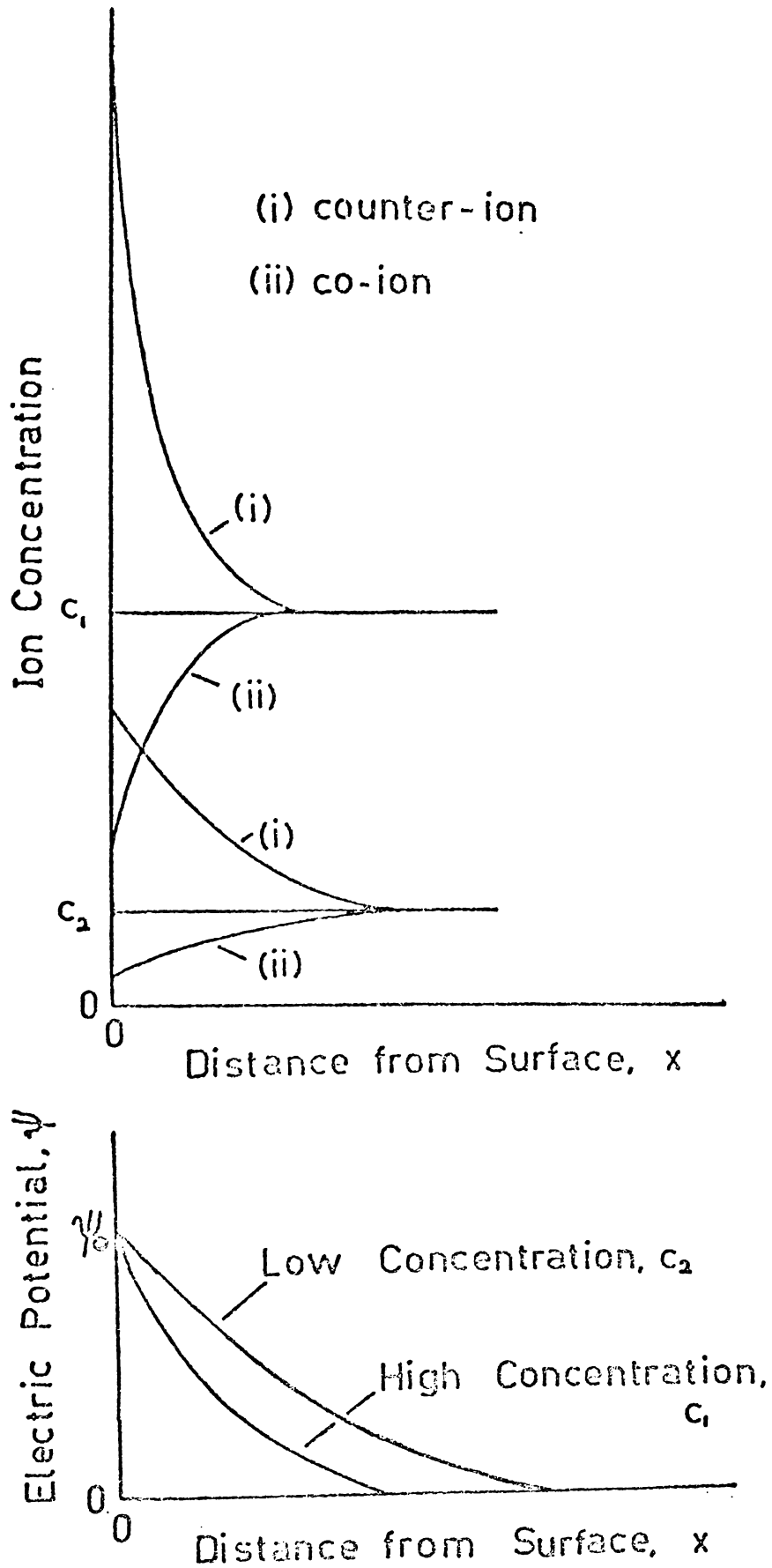


Figure 4.1. Ion concentrations and electric potential distributions in the Gouy-Chapman diffuse layer.

The potential distribution for $x > d$ follows the Gouy-Chapman theory whilst between the surface and $x = d$ it varies linearly from ψ_0 to ψ_d .

Electroneutrality means that;

$$\sigma_0 + \sigma_i + \sigma_d = 0 \quad (4.20)$$

where $\sigma_i = \int_0^d \rho \, dx$ and $\sigma_d = \int_d^\infty \rho \, dx$. σ_d , the charge in the diffuse part of the double layer, is also given by the Gouy-Chapman theory if in (4.16) ψ_0 is replaced by ψ_d .

Stern's equation to describe the adsorption of ions into the fixed or Stern layer, which can be derived from a consideration of the adsorption equilibrium between two phases of different electrical potential,⁹⁴ is;

$$\frac{c_i}{c_s} = \frac{N_0 - \sum_i c_i}{\frac{N}{M_h}} \cdot E_d^i \quad (4.21)$$

where N_0 is the total number of possible adsorption sites, N is Avogadro's number, M_h is the molecular weight of water, c_i is the concentration of species i in the Stern layer, $E_d^i = \exp\left[\frac{-z_i e \psi_d - \phi_i}{kT}\right]$ and ϕ_i is the specific adsorption potential for the ion. This latter potential accounts for the energy of interaction between the species and the surface which is not coulombic. (If ϕ_i is non-zero the species is said to be specifically adsorbed.) For $z:z$ electrolytes;

$$\sigma_d = \frac{zeN_0(E_d^+ - E_d^-)}{\frac{z}{c_s M_h} + E_d^+ + E_d^-} \quad (4.22)$$

where $E_d^+ = \exp\left[\frac{-ze\psi_d - \phi^+}{kT}\right]$, $E_d^- = \exp\left[\frac{ze\psi_d - \phi^-}{kT}\right]$ and ϕ^+ and ϕ^- are the specific adsorption potentials of the cation and anion respectively.

If only one ion is adsorbed significantly in the Stern layer (4.22) can be simplified. If in addition $c_i \ll N_0$ (4.21) transforms to;

$$\frac{c_i}{c_s} = \frac{N_o M_h}{N} E_d^i \quad (4.23)$$

At the aqueous/mercury interface the plane of specifically adsorbed ions is not the same as the plane of closest approach of the ions in the diffuse layer. This has been considered to be due to the presence of hydration layers. Grahame⁹⁵ considered the plane of specific adsorption, the inner Helmholtz plane or IHP, to be a distance β from the surface whilst the plane for closest approach of the ions in the diffuse layer, the outer Helmholtz plane or OHP, is a further distance $\gamma = d - \beta$ from the IHP. The diffuse layer is still described by the Gouy-Chapman model. An illustration of ion and potential distributions controlled by this system is shown in figure 4.2.

The electrochemical double layer may now be reasonably described for a $z:z$ electrolyte by the following equations provided that the interior potential of the solid is insignificant. From electrostatics the capacitance across the first region ($x = 0$ to $x = \beta$) gives;

$$\psi_0 - \psi_\beta = \frac{4\pi\beta}{\epsilon_1} \sigma_0 \quad (4.24)$$

and across the second region

$$\psi_\beta - \psi_d = \frac{4\pi\gamma}{\epsilon_2} (\sigma_0 + \sigma_\beta) \quad (4.25)$$

where ϵ_1 and ϵ_2 are the effective mean dielectric constants for the first and second regions respectively. The Gouy-Chapman theory can be applied to the double layer;

$$\sigma_d = - \frac{\epsilon k T}{2\pi z e} \sinh \left(\frac{ze}{2kT} \psi_d \right) \quad (4.26)$$

ϵ is the dielectric constant of the bulk liquid phase. The existence of electroneutrality across the region means;

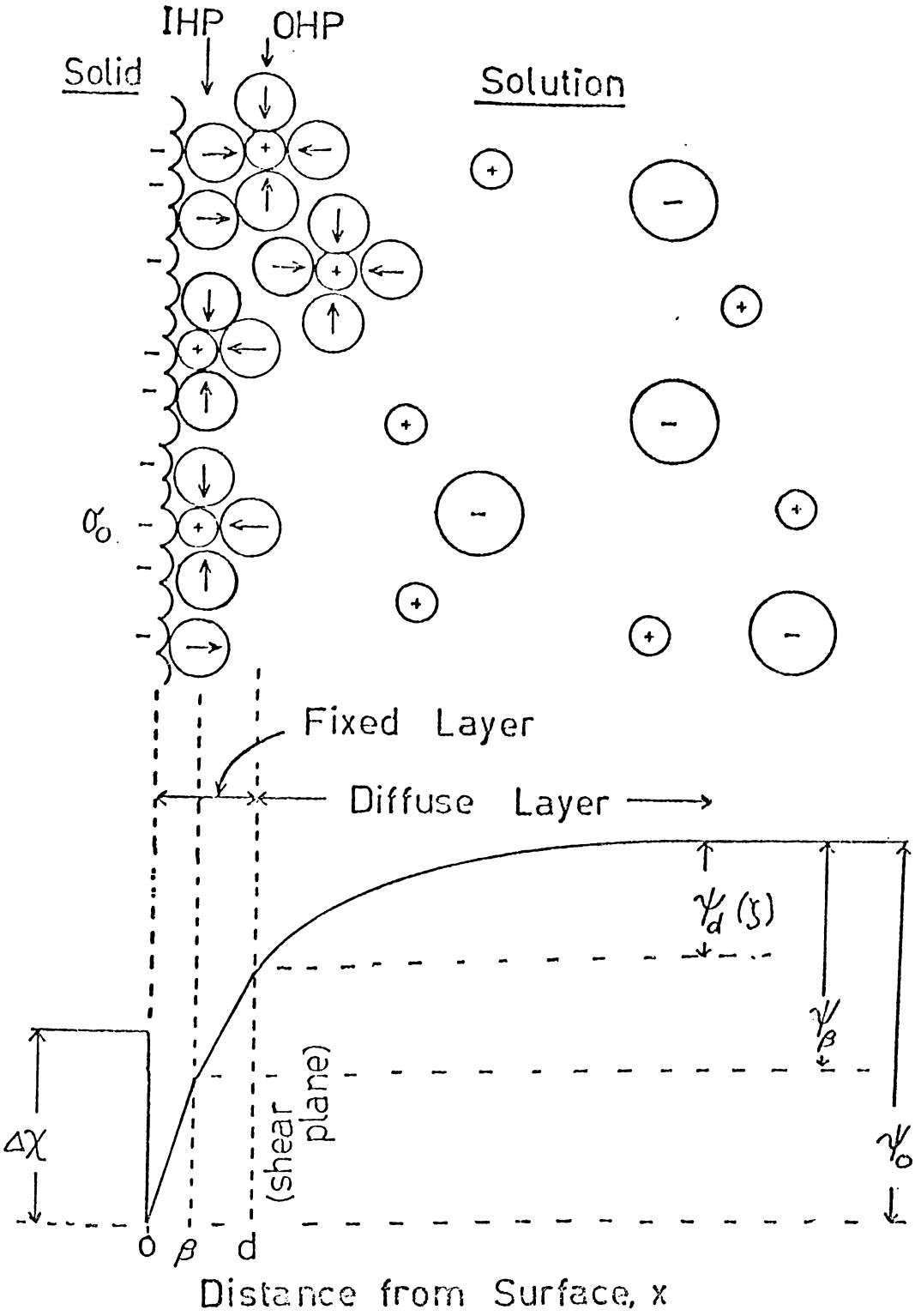


Figure 4.2. The structure of the double layer incorporating a Stern layer,

$$\sigma_o + \sigma_\beta + \sigma_d = 0 \quad (4.27)$$

whilst the charge in the IHP is given by the Stern equation for adsorption a distance β from the plane;

$$\sigma_\beta = \frac{zeN_o(E^+ - E^-)}{\frac{z}{c_s M_h} + E^+ + E^-} \quad (4.28)$$

where $E^+ = \exp\left\{\frac{-ze\psi_\beta - \phi^+}{kT}\right\}$ and $E^- = \exp\left\{\frac{ze\psi_\beta - \phi^-}{kT}\right\}$.

For any value of ψ_o and c_s the double layer parameters can then be determined. For a number of systems this model may be sufficient, particularly for low surface densities. However, a number of effects are ignored which may be of some significance in some other systems.

4.5.4 Some Further Aspects of the Double Layer

As is usually the case with most simple models a number of approximations have been made and some physical properties of the various species involved ignored in the double layer theory presented above. Amongst the assumptions made here are that the ions are non-polarisable, they are volume-less point charges, the dielectric constant of the fixed layer is constant and the Poisson equation holds for the surfaces considered. In general account needs to be taken of these properties only for sensitive measurements such as capacitance measurements of the mercury/aqueous interfaces.⁹⁶⁻⁹⁹ A significant correction sometimes arises from the discreteness-of-charge effect, caused by the finite volume of any adsorbed ion which must have about it a region devoid of charge whilst further away a mean charge is observed. This has been shown to produce a maximum in $|\psi_d|^{100}$ and in the potential of the double layer for silica¹⁰¹ with increasing surface potential for 2:2 and 3:3 electrolytes.

The change in solvation energy of an ion as it adsorbs has been

considered by Healy and co-workers¹⁰¹⁻¹⁰⁴ to be a significant term in the adsorption isotherm for divalent cations. They suggested that when cations adsorbed onto silica gel they may retain their primary solvation sphere but suffer severe disruption of the secondary hydration system (but see section 6.3.3). The absolute value of this free energy change, ΔG_{solv} , is dependent upon the relative differences between the dielectric constants of the solid, ϵ_0 , and the bulk, ϵ . (A better expression for ΔG_{solv} is given by Levine¹⁰⁵ who showed the necessity of including the dielectric constant of the hydration layer itself.) When $\epsilon - \epsilon_0 \rightarrow 0$, ΔG_{solv} is small but it may become important when the difference is large. Using James and Healy's¹⁰⁴ expression for ϵ_1 , the dielectric constant of the inner region of the fixed layer, (ϵ_{int} , p.75), it can be shown that if the Nernst equation (4.6) expresses the surface potential, the free energy of solvation change is constant except at high field strengths. With the modified Nernst equation (described in the next section) the change is constant throughout and so it can be considered to be a part of $\phi^\pm$ in (4.28).

Using (4.24) to (4.28) it is still not possible to calculate completely an adsorption isotherm for any ion, or completely describe the double layer, unless two of the variables are known. For any system the total amount of adsorbing ion present is usually known and so one further factor is required. This is commonly the surface potential which is directly determinable for completely polarisable electrodes or approximately available by calculation for reversible electrodes.

4.6 The Surface Potential of Hydrous Oxides

In section 4.3 it was shown that in some cases ψ_0 may be determined using the Nernst equation, (4.6), if the concentrations of

the p.d. ions are known. For silver iodide, replacing activities by concentrations will give (4.6) the form;

$$\Delta\psi_0 = 2.3 \frac{kT}{e} \Delta p_{Ag} = - 2.3 \frac{kT}{e} \Delta p_I \quad (4.29)$$

($p = -\log_{10}$). If the logarithm of the concentration of Ag^+ at the point where $\psi_0 = 0$, i.e., the PZC, is pAg_z , then;

$$\psi_0 = 2.3 \frac{kT}{e} (pAg_z - pAg) \quad (4.30)$$

For oxides of the form M_2O_z ;

$$\Delta\psi_0 = 2.3 \frac{kT}{e} \Delta p_M = - 2.3 \frac{kT}{e} \Delta p_O \quad (4.31)$$

If the equilibrium $M^{2+} + 2H_2O \rightleftharpoons M(OH)_2 + 2H^+$ is reached between the hydrous oxide surface and the solution then $\Delta p_M = z\Delta pH$. Again if the pH at the PZC is pH_z (assuming $\psi_0 = 0$ when $\sigma_0 = 0$, which is approached in the absence of specific adsorption);

$$\psi_0 = 2.3 \frac{kT}{e} (pH_z - pH) \quad (4.32)$$

This equation is consistent with the charging mechanisms for hydrous oxides given by (4.7).

Berubé and de Bruyn¹⁰⁶ have studied the applicability of the Nernst equation to hydrous oxides and concluded that it is a valid approximation provided the activity of the p.d. groups at the surface is constant, i.e., the total of neutral surface species at the PZC is low and most groups are charged.

A more general expression for the relationship between the pH and ψ_0 has been developed by Levine and Smith¹⁰⁷ who supposed that the p.d. ion adsorption isotherm could be described by a Stern-type equation where the potential felt by the adsorbed ion is the sum of the surface or macropotential, ψ_0 , and self atmosphere potentials, $\phi_0^\pm$, ϕ_0^+ and ϕ_0^-

are the self atmosphere (or specific adsorption) potentials for the p.d. ions H^+ and OH^- respectively. Their equation, in the form of Wright and Hunter,¹⁰⁸ is;

$$2.3\Delta pH = -\frac{e}{kT} \left\{ \Delta\psi_0 + \frac{\phi_0^+ + \phi_0^-}{2} \right\} - \frac{1}{2} \ln \left\{ 1 + \frac{\sigma_0}{N_0} \text{fn}(\sigma_0, y, N_0) \right\} \\ + \text{further power terms in } \sigma_0 \text{ and } y \quad (4.33)$$

y is a term relating to the proportion of charged groups and is unimportant for highly ionised surfaces, and N_0 is the total number of active ionisable surface groups. Hunter and Wright^{108,109} and Bowden et al.^{110,111} also doubted the reliability of direct application of the Nernst equation to weakly dissociated hydrous oxides because it overestimated ψ_0 . Consideration of the adsorption of p.d. ions obeying a Stern-type adsorption isotherm lead both groups to produce a similar relationship between ψ_0 , σ_0 and the p.d. ion concentration, which is;

$$\sigma_0 = \frac{eN_0 ([H^+] E_0^+ - [OH^-] E_0^-)}{\frac{1000}{M_h} + [H^+] E_0^+ + [OH^-] E_0^-} \quad (4.34)$$

where $E_0^+ = \exp \left\{ \frac{-e\psi_0 - \phi_0^+}{kT} \right\}$ and $E_0^- = \exp \left\{ \frac{e\psi_0 - \phi_0^-}{kT} \right\}$. ϕ_0^+ and ϕ_0^- may, for sparingly soluble hydrous oxides, be related to the acid and base dissociation constants of the neutral metal hydroxide and can be determined from the adsorption isotherms of the p.d. ions obtained from acid/base titration experiments¹¹² (see also section 4.7).

4.7 Surface Charge Determination and Point of Zero Charge

One of the most important parameters used to describe the state of the double layer at an electrolyte/solid interface is the point of zero charge (PZC)¹¹³ which is again defined as the electrolyte conditions necessary to make the surface charge zero, i.e., $\sigma_0 = 0$.

For a reversible electrode;

$$\sigma_0 = e(z^+ \Gamma_0^+ + z^- \Gamma_0^-) \quad (4.35)$$

where Γ_0^+ and Γ_0^- are the surface excess concentrations of the p.d. cation and anion respectively. If $z^+ = z^-$ then at the PZC $\Gamma_0^+ = \Gamma_0^-$. The activities of the p.d. ions responsible for σ_0 can usually be determined experimentally but criteria are needed to establish when the surface has no charge. From (4.24) if $\psi_\beta = 0$ then when $\psi_0 = 0$, $\sigma_0 = 0$. This condition is only approached if $\sigma_\beta = 0$, i.e., there is no specific adsorption in which case from (4.25) $\psi_d = 0$. In the absence of specific or non-equivalent specific adsorption, at the PZC all potentials associated with the surface are zero.

If $\psi_d = 0$ then the zeta potential, ζ , (see Chapter Nine) with which it enjoys a direct relationship, will also be zero so that electrokinetic phenomena associated with ζ will themselves be zero or pass through minima or maxima at this point. The negative logarithm (base 10) of the concentration of p.d. ions at this point is defined as the isoelectric point or IEP*.¹¹⁴ Some electrokinetic properties of colloids are discussed in Chapter Nine.

Again if $\sigma_\beta = 0$ then from (4.27) $\sigma_0 = -\sigma_d$ so that from (4.26) $|\sigma_0| \propto c_s^{\frac{1}{2}}$. This relationship is the basis for potentiometric titration determinations of the surface charge and PZC since σ_0 is dependent upon the p.d. ion concentration. If it can be measured plots of the amount of p.d. ion adsorbed against the p.d. ion solution concentration at various strengths of indifferent electrolyte ($\phi^\pm \rightarrow 0$) should intersect at the PZC. These plots can then be calibrated in terms of σ_0 .

*It is important to distinguish between the IEP ($\zeta = 0$) and the PZC ($\sigma_0 = 0$). Generally in the absence of specific adsorption, or providing that the specific adsorption potentials of both the cation and the anion are equal, i.e., $\phi^+ = \phi^-$, then the IEP and the PZC coincide. However, this distinction is not always made in the literature and the two have been frequently confused.

An alternative picture may be visualised if the surface is considered to have ion exchange properties. For any sample, increasing electrolyte concentration results in a release of p.d. ions, predominantly cations for $\sigma_0 > 0$, predominantly anions for $\sigma_0 < 0$ and roughly equal for $\sigma_0 = 0$. The release is proportional to the electrolyte concentration and so when it is reduced $|\sigma_0|$ will be greater. At the PZC there is no change in the bulk concentration of the p.d. ions with electrolyte strength so that the PZC may be determined by adding electrolyte at different p.d. ion concentrations until the conditions at which the p.d. ion concentrations do not change are found.

The surface charge of soil components particularly has been determined by following the adsorption of an indifferent salt ($\phi^+ \rightarrow 0$ or $\phi^+ = \phi^-$) such as sodium chloride which provides the counter-ions to the surface charge.¹¹⁵ At the PZC the adsorption of both cation and anion will be equal. Two situations are likely here:

- (i) No adsorption in the Stern layer. This has frequently been assumed for the adsorption of salts such as sodium chloride but it may apply only to surfaces such as mercury or perhaps the silver halides. Here $\sigma_\beta = 0$ so;

$$\sigma_0 = \sigma_d^+ + \sigma_d^- = \sigma_d \quad (4.36)$$

where σ_d^+ and σ_d^- are the positive and negative components of the charge in the diffuse layer respectively. At the PZC $\sigma_0 = 0$ and $\sigma_d^+ = -\sigma_d^-$. Differentiation of the surface charge into positive and negative components has been made,³⁰ i.e., $\sigma_0 = \sigma_o^+ + \sigma_o^-$ so that $\sigma_o^+ + \sigma_d^- = 0$ and $\sigma_o^- + \sigma_d^+ = 0$. This assumes that the positive and negative surface sites are discrete and they are not exhaustively self-neutralising. This is a reasonable assumption provided the surface is ionised at the PZC or is composed of more than one surface

group with different p.d. ion interactions.

- (ii) Significant adsorption in the Stern layer. Most hydrous oxides adsorb small cations and anions into the fixed layer (see Chapter Seven). In this case equivalent adsorption of electrolyte ions will depend upon their having the same specific adsorption potential. Now however $\sigma_o^+ + \sigma_d^- + \sigma_\beta^- = 0$ and $\sigma_o^- + \sigma_d^+ + \sigma_\beta^+ = 0$ at the PZC. Before this method can be used it should be verified that the specific adsorption potentials for both cation and anion of the electrolyte are equal.

A typical surface charge-pH plot for a hydrous oxide is shown in figure 4.3 for a situation without specific adsorption, i.e., the cation and anion of the electrolyte had similar (low) specific adsorption potentials. At high electrolyte strength the relationship is nearly linear. $\partial\sigma_o/\partial\psi_o$ is a measure of the surface capacitance and as ψ_o is near linear with pH it can be seen that the capacitance will pass through a minimum at $\sigma_o = 0$, the PZC, a feature of both reversible and completely polarisable surfaces.

Adsorption of cations with a high specific adsorption potential (specific adsorption) causes a shift in the surface charge by decreasing its positive contribution. Consequently a greater solution activity of the p.d. cation will be found at the PZC. A conceptual view of this may be aided by recognising that specific adsorption results in the adsorbed ion approaching a state like that of a p.d. ion but still being quite distinct. This effect is evident not only in the position of the PZC but also in the Esin-Markov coefficient, D_{EM} , which is a measure of the p.d. ion concentration change required to keep σ_o constant for a ten-fold change in the concentration of the electrolyte.¹¹⁶ For cation adsorption onto oxides from a z:1 electrolyte this is;

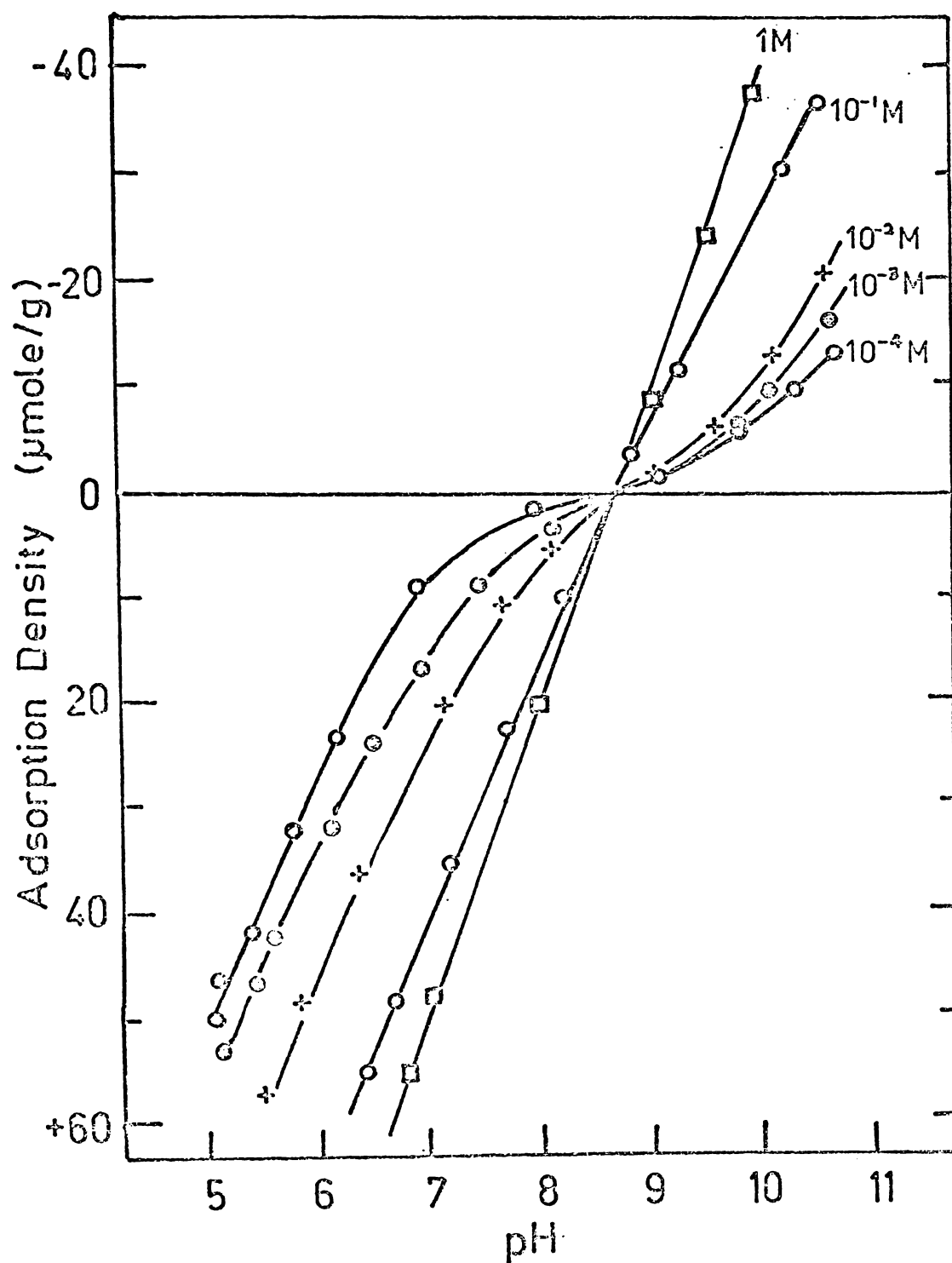


Figure 4.3. Adsorption density of p.d. ions on ferric oxide as a function of pH and electrolyte concentration. (Redrawn from ref. 113.)

$$D_{EM} = \left[\frac{dpH}{d \log a^{\pm}} \right]_{\sigma_0} = 1 - \frac{z+1}{z} \left[\frac{\partial \sigma^+}{\partial \sigma_0} \right]_{a^{\pm}} \quad (4.37)$$

where $a^{\pm}$ is the salt activity and σ^+ the charge contribution of the cation. In the absence of specific adsorption for $z = 1$, when σ_0 is large and negative $\partial \sigma^+ / \partial \sigma_0 = 1$ (all the charge is balanced by cations) and so $D_{EM} = -1$ whilst at high positive σ_0 there are no adsorbed cations, $\partial \sigma^+ / \partial \sigma_0 = 0$ and $D_{EM} = 1$. At the PZC anion and cation contribute equally to the neutralising charge, $\partial \sigma^+ / \partial \sigma_0 = 0.5$ and $D_{EM} = 0$. This is also seen in the plot, figure 4.3. When a cation adsorbs specifically, its specific adsorption potential is relatively large compared with that of the anion, the contributions to σ_0 at the p.d. concentration extremes will not be changed but in the region of the PZC the cation contribution will exceed that of the anion, i.e., $\partial \sigma^+ / \partial \sigma_0 > 0.5$, $D_{EM} < 0$ and so for oxides the PZC will move to lower pH. Adsorption of divalent cations will be expected to give $D_{EM} \rightarrow 1$ at low pH and $D_{EM} \rightarrow -0.5$ at high pH. Frequently divalent ions are specifically adsorbed up to a limiting value after which further adsorption appears non-specific.¹¹⁶ This results in a decrease of the PZC and σ_0 for low concentrations which is not maintained at higher concentrations, causing, in turn, a congregation of the σ_0 -pH plots for various concentrations of the electrolyte at low pH. Examples of this have been reported by Keng and Uehara¹¹⁷ for both divalent cations and anions.

4.8 Further Aspects of the Diffuse Part of the Double Layer

4.8.1 The Potential of the Diffuse Layer

In general the potential at any point in the diffuse layer can be represented, at least for 1:1 electrolytes below $10^{-2}M$,^{118,119} by the Gouy-Chapman solution to the Poisson-Boltzmann equation (4.17) or the

approximation (4.18) but with replacement of ψ_0 by ψ_d and x by $(x - d)$ so that (4.18) would become;

$$(x - d)\kappa = \ln \frac{\psi_d}{\psi} \quad (4.38)$$

With multivalent ions and at higher concentrations a number of corrections must be introduced but the complexity of these is excessive particularly as the effects, image forces, ion volumes, dielectric constant variation, electrostriction, must all be incorporated in the manner used by Levine and co-workers^{100,118} for the properties of the inner region (section 4.5.4). At least part of the difficulty, especially with the dielectric constant and the viscosity, arises because for simplicity, the property is regarded as a step function in x rather than varying continuously. For the diffuse layer discussions in this thesis the simple Gouy-Chapman distribution will be sufficient. (See also section 4.8.3.)

4.8.2 The Effect of Specific Adsorption on the Diffuse Layer

As ψ , in (4.38), is a function of ψ_d , the potential at the OHP, it will reflect all the charges at the surface and within the IHP. With no Stern layer adsorption only the surface charge will be effective so that for reversible surfaces the diffuse double layer potential and diffuse layer ion distribution will depend upon the p.d. ion and electrolyte concentrations. Stern layer adsorbed ions will, however, either enhance (if they are co-ions), or reduce (if they are counterions), the effective surface charge felt at the diffuse layer. If sufficient adsorption of counterions occurs there may be a reversal of the nett surface charge as observed in the diffuse layer which means a considerable rearrangement of the counterions in the diffuse layer must also occur.

4.8.3 The Diffuse Layer at a Curved Surface

For a surface of radius of curvature r_0 the form of the

Laplacian operator used to solve the Poisson equation (4.8) will be acceptable provided that r_o is considerably greater than the diffuse layer, i.e.;

$$\kappa r_o \gg 1 \quad (4.39)$$

a condition which will not be satisfied for small colloids in dilute electrolytes but which usually holds in more concentrated solutions and for larger bodies. A similar condition can also be applied to the fixed layer near the surface but as d is commonly of the order of 1 nm or less few colloids would not satisfy the requirements for approximation to a plane. When (4.39) does not hold it becomes necessary to solve the Poisson-Boltzmann equation (4.8) using the three dimensional Laplacian operator $\nabla^2 = d^2/dx^2 + d^2/dy^2 + d^2/dz^2$, a much more complicated procedure which is discussed in the review by Dukhin.⁸⁶ This will not be considered here but it will be pointed out that its neglect may produce errors when quantitative diffuse layer calculations are carried out for electrolyte solutions of less than $10^{-2}M$ when $r_o \sim 50$ nm or less.

4.8.4 pH in the Diffuse Layer

As the pH is determined by the activity of ionic species in the diffuse layer it will be influenced by the nett effects of the surface and Stern layer charges via the potential at the OHP, ψ_d . If the nett surface charge is positive the diffuse layer will appear depleted of H^+ when compared with the bulk solution whilst negative surfaces will attract H^+ and repel OH^- in this same zone. Thus the pH in the diffuse layer will be moved from its value in the bulk solution in the direction of the IEP.¹²⁰

In the diffuse layer at a distance x from the surface, at which point the potential is ψ , using (4.9) the pH, pH_x , will be given

by;

$$\text{pH}_x = \text{pH} + \frac{e\psi}{2.3kT} \quad (4.40)$$

ψ can be found from (4.17) if ψ_d is substituted for ψ_0 .

The difference in the potential at a point in the diffuse layer will depend upon the thickness of the double layer, i.e., $1/\kappa$, the position of the point of interest in the diffuse layer and the potential difference between the bulk solution and the OHP. Thus for concentrated electrolyte solutions with compressed diffuse layers the difference will be small even at pH away from the IEP. For extensive diffuse layers such changes may be significant, particularly for adsorbed species such as enzymes whose activity may then be altered.^{121,122}

CHAPTER FIVE

SURFACE CHARGE STUDIES AND
THE POINT OF ZERO CHARGE

5.1 Introduction

In Chapters Two and Three it was shown that allophane is basically an aluminosilicate with variable coatings of aluminium hydroxide and perhaps iron(III) hydroxy species. These hydroxide components give the whole surface in aqueous suspension some of the characteristics of a pure hydrous oxide. Thus allophane might be expected to behave like these substances whose surface chemistry is more thoroughly understood. The development of surface charge on hydrous oxides, its variation with pH, and methods for its determination have been discussed in sections 4.4 and 4.7. In addition, the point of zero charge (PZC) was defined and the difference between it and the isoelectric point (IEP) was stressed. Because they do not necessarily coincide an attempt will be made to distinguish between values reported indiscriminately as PZC or IEP in the literature (e.g., in ref. 123) by using PZC only for zero points determined from ion adsorption experiments, whether with potential determining (p.d.) or "non-specific" ions, and IEP for the zero point from electrokinetic processes. Values of PZC's, and the influences of various phenomena upon them are stressed because of the relevance they have to ion adsorption processes and the total particle surface charge.

5.2 The Points of Zero Charge of some Hydrous Oxides

Parks^{123, 124} has collected the points of zero charge and the isoelectric points of a number of oxides, hydroxides and oxide minerals. He has shown that the values of these points correlate with other properties of the matrix metal such as its ionic radius, crystal field stabilisation energy, and the difference in the acid and base dissociation constants of the surface hydroxyl groups. These were fitted to an empirical equation which predicted the PZC with reasonable reliability. The above properties show the effects of metal coordination number and the ratio of bonds exposed to the solution to those involved in the structure. They also show the degree of surface hydration which must effect the acid/base interactions. It is notable that these properties are also those associated with solubility and it has frequently been observed that the PZC coincides with, or is close to, the point of minimum solubility.

A further number of PZC values have been collected by Ahmed (p.438).⁸⁸ A number of these, as well as some from Parks,¹²⁴ are reproduced in Table 5.1.

The most important values here are those for silica, the various aluminous systems and the materials of mixed composition. The acidic nature of silica is apparent from its low PZC. Furthermore, the plots of the surface charge, σ_0 , against pH for this material tend to approach $\sigma_0 = 0$ at low pH and do not go above this even at pH 1.⁸⁸ Parks has shown that for a binary mixture of two independent sites the PZC will be expected to be the site concentration weighted mean provided σ_0 for each varies linearly with the concentration of the p.d. ions. If the PZC's of the two materials were sufficiently different separate regions of positive and negative charge would occur in suspensions of pH near the PZC of the mixture. Parks' predictions for ortho-aluminium silicates were reasonably accurate but

Table 5.1 The Points of Zero Charge of some Hydrous Oxides and Similar Materials. (Taken from refs. 88, 123 and 124.)

oxide	form	PZC
SiO ₂	quartz	2.7 to 3.0
SiO ₂	hydrous sol	1.8
Fe ₂ O ₃	precipitate	8.3
α-Fe ₂ O ₃	haematite	9.0
Al ₂ O ₃	alumina	7.8
α-Al ₂ O ₃	amorphous	9.1
α-Al(OH) ₃	gel	9.25
Al ₂ O ₃	tetrahedral	4.7
SiO ₂ /Al ₂ O ₃	hydrous co-gel	
$\frac{\text{Si}}{\text{Si} + \text{Al}} = 0.40$		6.2
0.50		5.5
0.58		4.2
0.44 (dried)		6.2*
MgO		12
As ₂ O ₅		0.4

*From reference 125.

for more complex chains and sheets they were less reliable. The co-precipitates of silica and alumina are complicated by the presence of both tetrahedral and octahedral aluminium. This introduces a negative charge to the structure from isomorphous substitution; i.e., from Al(III) replacing Si(IV). Perrott¹²⁵ found good correlation between the PZC's of a number of amorphous aluminosilicates, using Schofield's method for surface charge determination, and the IEP's of similar materials reported by Parks.¹²³ Mechanical mixtures of silica and aluminium also behaved in the manner predicted but at high

silica content alumina had a disproportionate effect.¹²⁶ This was probably because the increasing solubility of aluminium with decreasing pH, particularly near the silica PZC, allowed a distribution of aluminium hydroxide over the silica surface (see section 7.3.7).

Drying and heating hydrous oxides has been found to cause large changes in their PZC's which have not always been readily reversed.¹²⁴ Dehydration may force the incorporation of entrained salts and this would alter the surface properties. (A similar irreversible change has also been found for the clay mineral kaolinite.¹²⁶) Thus it would be expected that the surface properties of a clay after drying may not be the same as those it displays in the soil.

Specific adsorption of cations by hydrous oxides gives a general movement of the surface charge to more negative states whilst the same type of adsorption of anions causes a movement toward more positive values and a rise in the value of the PZC. This has been discussed in section 4.7.

5.3 Surface Charge and Point of Zero Charge of Soils and Clays

The importance of surface charge in reactions of soils has long been recognised but not well studied. As by far the greatest proportion of the surface area of a soil is associated with its clay fraction the nett surface charge will depend mostly upon this part. In this discussion the influences of organic matter, which are important in many soils, are ignored.

The external surface of a crystalline clay mineral will be a tetrahedral silica sheet or an octahedral aluminium sheet, or in some cases both. The silica sheets, such as those of the three layer clay mineral montmorillonite or the micas, are comparatively unreactive as they contain few hydroxyl groups and these, like those of silica itself, are not readily protonated; nor are they easily deprotonated or

suitable for hydroxyl adsorption except at higher pH. At the ends of these sheets a larger number of hydroxyl groups do occur, from so-called broken bonds, and these are more susceptible to acid/base reactions.^{127,128} A large negative charge is usually present within the lattice from isomorphous replacement, usually of aluminium for silicon. Generally adsorbed, but freely exchangeable, cations occur in the fixed layer at the surface to neutralise this internal structural charge. The nett surface charge of these minerals is roughly constant over a wide pH range unless the acid or base strength becomes strong enough to involve the surface in ionisations, such as silanol dissociation at pH greater than 6.¹²⁹ Because their surface charges have not been dependent upon pH or electrolyte concentration these materials have been called "constant charge" minerals.

Minerals such as kaolinite and halloysite have, in addition to a surface of silica, a surface of octahedral aluminium with its associated hydroxyl groups. As the reactivities of these groups are dependent upon both the pH and the electrolyte concentration, and furthermore the Nernst equation, (4.6), might be applied to them, they are known as the "constant potential" minerals. The surface charge of this class of substance, which includes the hydrous oxides, varies continuously with pH as the hydroxyl groups undergo acid/base dissociations. However both kaolinite and halloysite also have a large negative charge contribution from isomorphous replacement. It has been suggested that the charge sites on kaolinite are discrete as the charge increases with electrolyte concentration. According to Schofield¹¹⁵ this arises from reduction of thickness of the double layer about any site and prevention of overlap of the fields of opposite charge sites and their consequent mutual reduction in effectiveness.¹³⁰ This idea is somewhat at variance with the double layer theory which suggests that more ionisation occurs; when an electrolyte increases in strength

it is to be expected that any ionisable material present will become more ionic, like its surroundings, and not merely be able to more effectively display the same ion content.

Hydrous iron(III) oxides gave a pH dependent contribution to the surface charge of a predominantly illitic soil clay¹¹⁵ and to kaolinite mixtures¹³¹ but played little part in the charging of allophanic clays according to Fieldes and Schofield.³⁰ Upon acid leaching kaolinite experienced a decrease in surface charge which was associated with the loss of substantial amounts of aluminium.¹³² If aluminium was specifically adsorbed, in the same manner as, say, calcium is said to be, its removal would have been expected to bring about an increase in the PZC. The aluminium associated with kaolinite is in a hydrolysed state and should be considered to be a part of the surface, not an electrostatically adsorbed species. Its removal would cause the loss of a positive charge component and expose underlying silicate, a more acidic fraction. Similarly the adsorption of silicate by goethite has been seen to reduce this oxide's surface charge.¹³³ The influence of an adsorbed species on surface charge will depend upon its relation to the surface. Adsorption of a hydrolysable ion that can be readily charged by adsorption of H^+ or OH^- will give charge characteristics of its own hydrous oxide to the surface.

In general, adsorption studies of allophane show PZC's between pH 5 and 6 with rapidly increasing charge away from this region. Acid/base titration of a New Zealand allophane in 0.2 M sodium chloride gave a near linear response to the amount of acid or base consumed in the pH region 4 to 8.³⁰ Imogolite, like the synthetic aluminosilicates, has been found to have an increasing positive, or decreasing negative, surface charge with increasing aluminium content. This may be correlated not only with the difference in the PZC's of the two constituents but also with the increasing contribution of octahedral

aluminium at the surface and the decreasing contribution from tetrahedral matrix aluminium.¹³⁴ Allophanes did not give a similar correlation. The PZC's of a number of clay minerals are given in Table 5.2.

Table 5.2 Points of Zero Charge and Isoelectric Points of some Clay Minerals

clay mineral	IEP	PZC	method*	Ref.
kaolinite	3.3		em	132
		2.8 - 3.0	titr	126
		3	ads	135
montmorillonite	3		em	136
		< 4	ads	137
imogolite	9 - 10		em	35
allophane		> 7	ads	137
		5 - 6	ads	30
		5.8	ads	138
		6.2	ads	139
		6.5	floc	140
	6.7		em	141
	5.8		em	35

* em, electrophoretic mobility; titr, potentiometric titration; ads, salt adsorption; floc, flocculation.

A number of reports of the surface charge and PZC's, determined by potentiometric titration, of some ash derived soils from the tropics have recently been published.^{117, 142, 143} In such soils of low organic and high aluminium or iron(III) content the apparent PZC is usually above 4 and may exceed 6. In soils low in both these elements but containing more siliceous material or organic matter the apparent PZC's tend to be below 4. These determinations were made by the slow

batch method but no consideration of any dissolution processes was made. It will be seen later in this chapter that although this effect may not necessarily change the PZC greatly it does have large effects upon the apparent surface charge. The surface charges of two soils from Hawaii were also determined by salt adsorption and these gave similar PZC's to the titration method.¹⁴³ This was also found for kaolinite.¹³⁵

5.4 An Experimental Study of the Surface Charge of some Materials by Potentiometric Titration

5.4.1 Introduction

Determinations of the PZC's of allophanes have previously relied upon the methods of equivalent adsorption of a cation and an anion with a low specific adsorption potential, i.e., "non-specifically" adsorbed ions. This does not satisfactorily illustrate the interactions of the p.d. ions with the surface and so a procedure that could supply this information was sought. The titration method of Parks and de Bruyn¹¹³ was chosen after the fast titration method of Berubé and de Bruyn¹⁰⁶ had been used and found to have some shortcomings when applied to allophane.

5.4.2 Experimental Determination of Surface Charge by Titration

The titration method for surface charge determination was adapted for oxides by Parks and de Bruyn.¹¹³ Later Berubé and de Bruyn considered two methods of acid/base titration.¹⁰⁶ The slow method allowed sufficient time for complete equilibrium to be reached and pH to become constant although this might not be for several days. The fast technique allowed only a few minutes between additions of acid or base and consequently permitted only a quasi-equilibrium of the surface metal-aquo complexes to be attained and not the slow redistribution of the matrix caused by dissolution and reprecipitation of the oxide

components. The differences in the results between the two methods for well characterised sparingly soluble oxides were not very great¹⁰⁶ but with more soluble materials such as zinc oxide there were significant slow processes which could be interpreted in terms of ion exchange between hydroxide and anions incorporated in the oxide during preparation.¹⁴⁴ To obtain the true surface charge it was necessary to correct for the dissolution of the oxide which was done by considering a mass balance of the added titrant.

When an aliquot ΔV of a strong acid of molarity x is added to a suspension of an oxide MO in an electrolyte a total balance of the material is;

$$x \cdot \Delta V = X + Y + A \cdot \Delta \Gamma_O^+ \quad (5.1)$$

where X is the increase in the total free acid given by;

$$X = (V + \Delta V) \cdot ([H^+]_f - [OH^-]_f) - V([H^+]_i - [OH^-]_i) \quad (5.2)$$

V is the suspension volume, i and f refer to initial and final states respectively. The amount of acid consumed in solubility changes for the oxide is given by;

$$Y = (V + \Delta V) \cdot (\sum_j z_j [MHO_j]_f) - V(\sum_j z_j [MHO_j]_i) \quad (5.3)$$

where MHO_j represents all species of the metal involved in the solution equilibrium including hydrolysis products (for ZnO these are Zn^{2+} , $ZnOH^+$, $Zn(OH)_3^-$, etc.).¹⁴⁴ The final term in (5.1) gives the total amount of acid actually adsorbed onto the surface since A is the total surface area of the sample and $\Delta \Gamma_O^+$ is the change in the specific surface excess of the adsorbed proton. X can readily be determined by pH titration of blank electrolyte solutions, whilst Y may be calculated if the concentrations of all species MHO_j are known or can be calculated.

5.4.3 Rapid Titration Procedure

5.4.3.1 Method

A sample of the Ohaupo allophane in the sodium form was treated twice with 0.1 M sodium chloride by stirring the suspension for 24 hours and centrifuging. The clay was then washed with twice-distilled water until the supernatant liquid from the centrifuging gave no precipitate when mixed with 0.1 M silver nitrate. The clay was then resuspended in the required electrolyte, stirred overnight, and a known aliquot taken into a pyrex reaction vessel maintained at $25 \pm 0.2^{\circ}\text{C}$ and stirred with a teflon-coated magnet. Moist carbon dioxide-free nitrogen was passed through the suspension for one hour; during the course of the titration an atmosphere of nitrogen was maintained above the suspension. Known aliquots of 0.1 M hydrochloric acid were added with a Radiometer Autoburette ABU11 every 2.5 minutes. Two minutes after the addition the stirring was halted (the pH meter fluctuated during stirring) and the pH determined with Radiometer K401 calomel and G202C glass electrodes connected to a Radiometer 26 pH meter.

The amount of H^{+} adsorbed was taken as the difference between the amount added and the amount required to induce the same pH in an equivalent solution of the electrolyte alone.

5.4.3.2 Results and Discussion

The consumption of acid with pH by the clay is shown in figure 5.1. This amount was found to vary with the aliquot size and time between additions. The latter was kept constant but the former needed to be increased at various pH values. The titration curves did not have a common point of intersection although crossover did tend to occur in the region 4.7 to 4.9. Because of the pH variations with time and the consequent difficulty in comparison between the different curves an alternate method was sought. The individual sample or batch

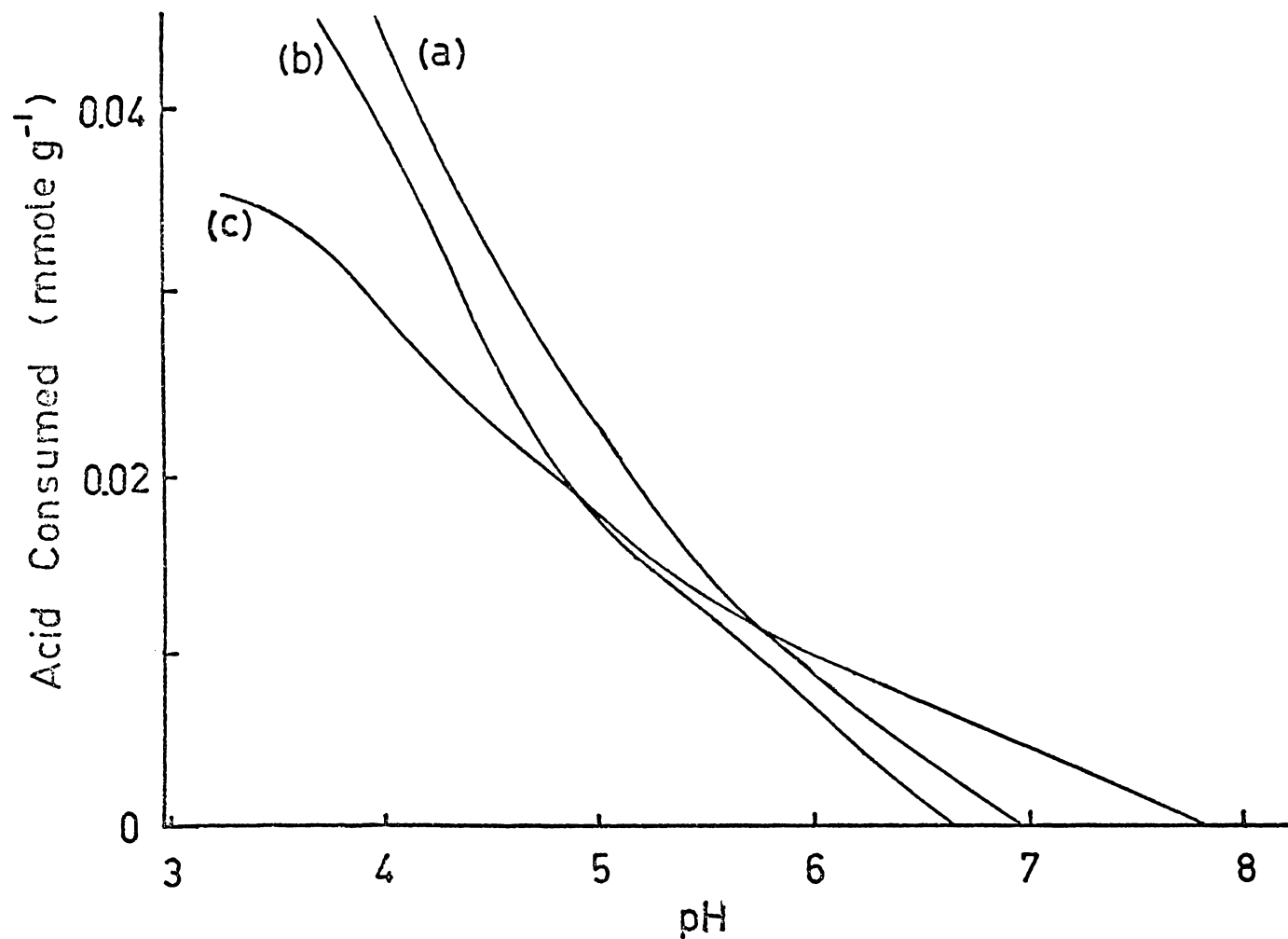


Figure 5.1. Consumption of acid during titration of Ohaupo allophane as a function of pH and electrolyte concentration. (a) 0.1 M, (b) 1 M, (c) 0.001 M.

procedure, which is based upon the method of Parks and de Bruyn,¹¹³ allows comparison of the various samples after the same time has elapsed from preparation and avoids some of the uncertainty experienced with the "rapid" method.

5.4.4 Batch Procedure

5.4.4.1 Method

Aliquots of clay suspensions, electrolyte and either standard

0.1 M sodium hydroxide or hydrochloric acid were taken in a plastic centrifuge tube, made up to 10 ml with fresh twice-distilled water, sealed and mixed by "end-over-end" rotation at 6 rpm. After desired time intervals the pH of the suspension was determined with a Radiometer GK2321C combination electrode and model 28 pH meter. In some instances the clay was removed by high speed centrifugation and the aluminium concentration of the supernatant liquid measured using the solochrome cyanine R method.¹⁴⁵

The amount of acid or base consumed was again taken as the difference between the amount added and the sum of the amount required to induce the same pH in an equivalent electrolyte solution. In those cases when dissolved aluminium was determined the amount of acid or base consumed was calculated using (5.1), i.e., the difference between the amount added and the sum of the amount required to induce the pH change and the amount required to account for the quantity of free aluminium. The last quantity was calculated from the amount in solution and the distribution between the forms Al^{3+} and AlOH^{2+} at the sample pH using the equilibrium constants taken from Sillén and Martell.¹⁴⁶ The dissolution of other species was not considered important.

5.4.4.2 Results and Discussion

The amount of acid or base consumed by the same sodium form clay as used for the rapid titration procedure is shown in figure 5.2.

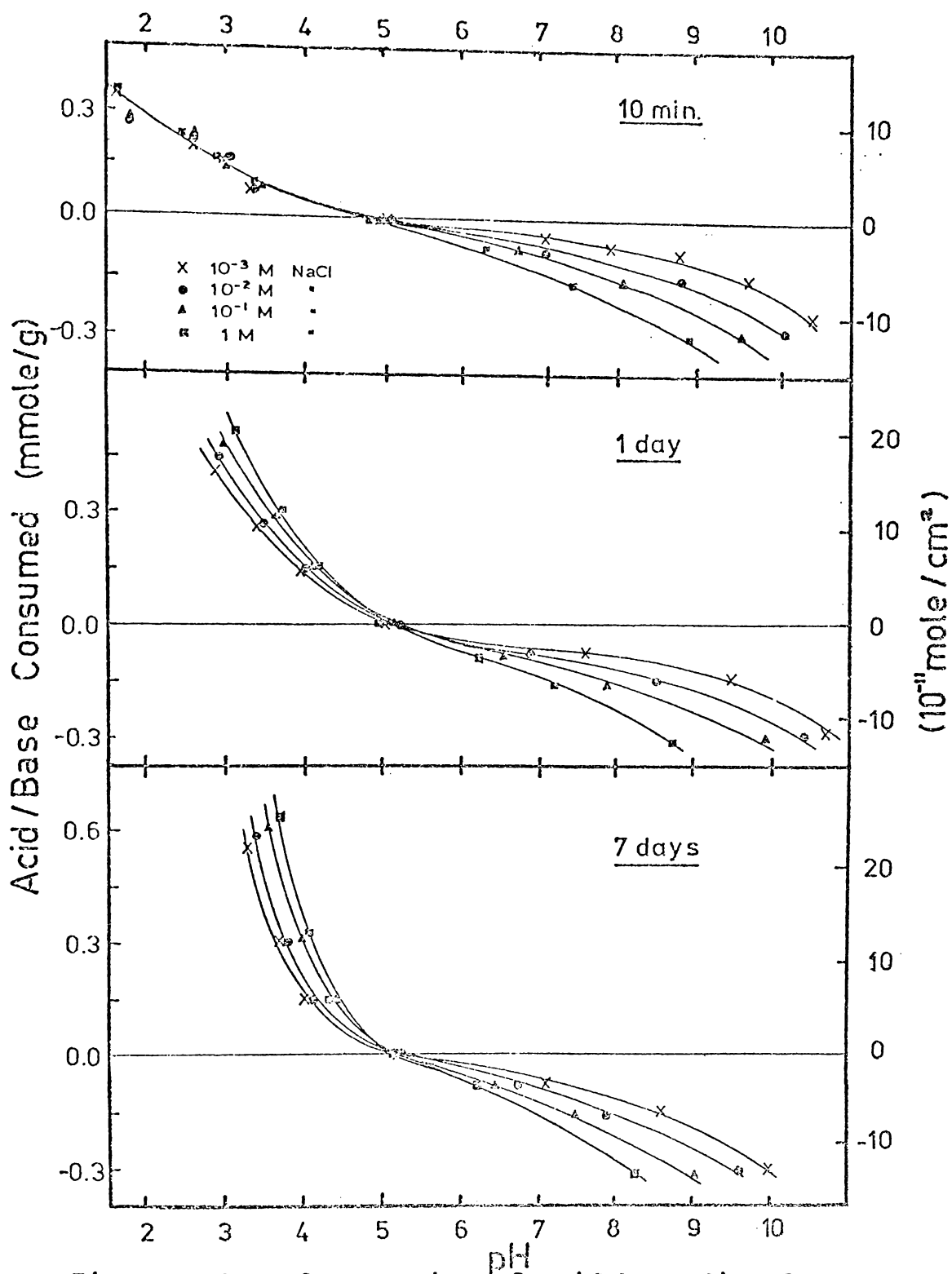


Figure 5.2. Consumption of acid by sodium-form Ohaupo allophane at various times after interaction as a function of pH and electrolyte concentration. Clay concentration 3.1 g/l.

The point of intersection was initially near 4.5 but an exact value cannot be readily ascribed. Upon ageing there was a small increase and the apparent PZC approached 4.8. As time progressed acid particularly was consumed, probably mostly by dissolution of aluminium although some adjustment with the interior of the material may occur as is evident by the slow changes occurring around pH 6 to 8 where aluminium hydroxide dissolution was slight. (The concentrations of aluminium found for this clay after equilibration for 24 hours are shown in figure 3.1.) Before dissolution was much advanced, i.e., after 10 minutes, the plots were somewhat similar to those observed in the presence of a divalent (specifically adsorbing) cation for some tropical subsoils,¹¹⁷ with an apparent Esin-Markov coefficient (section 4.7) approaching 1 at high pH and 0 at low pH. It appeared possible that some cation present was being specifically adsorbed. To check this proposition a sample of the clay was washed with 0.1 M hydrochloric acid several times, including an overnight stirring, prior to 6 washes with fresh twice-distilled water. This procedure removes most exchangeable free cations and should induce an increase in the PZC if specifically adsorbing cations had been removed. Instead, intersection of the curves did not occur at all (fig. 5.3). Ageing of this suspension in distilled water in a closed vessel with stirring slowly reduced this effect and after two weeks its behaviour had almost returned to that of the parent material (fig. 5.4a). Again a sharp increase in acid consumption became apparent at low pH this being due predominantly to aluminium dissolution. The apparent PZC of this aged material was near 4.4 which is a movement in the opposite direction to that expected if cations with high specific adsorption potentials had been removed but it is that observed when high PZC components are removed from the surface leaving low PZC siliceous matter.¹³² In this case the high PZC component would be

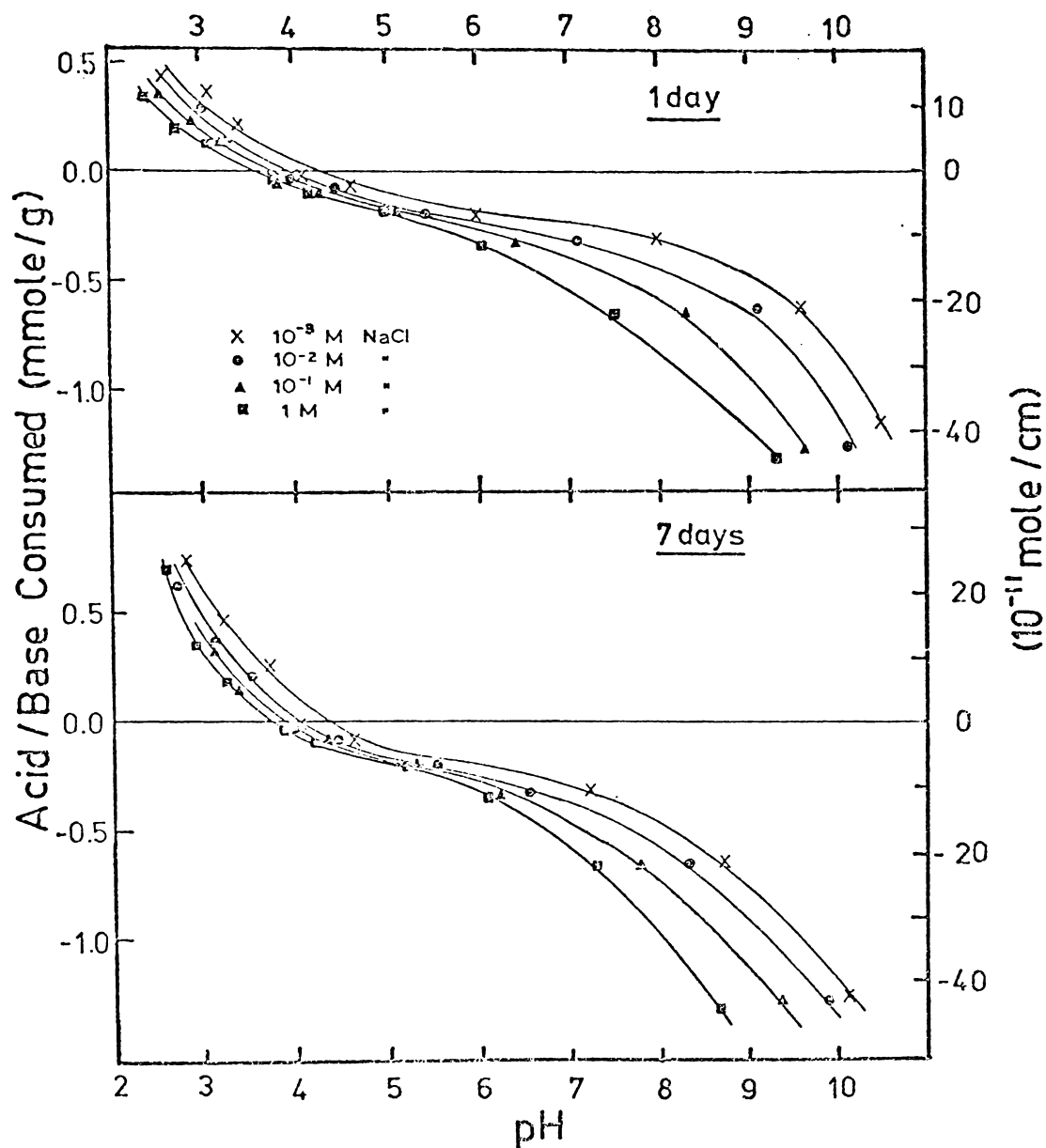


Figure 5.3. Consumption of acid and base by freshly acid-washed Ohaupo allophane at various times after interaction as a function of pH and electrolyte concentration. Clay concentration 2.95 g/l.

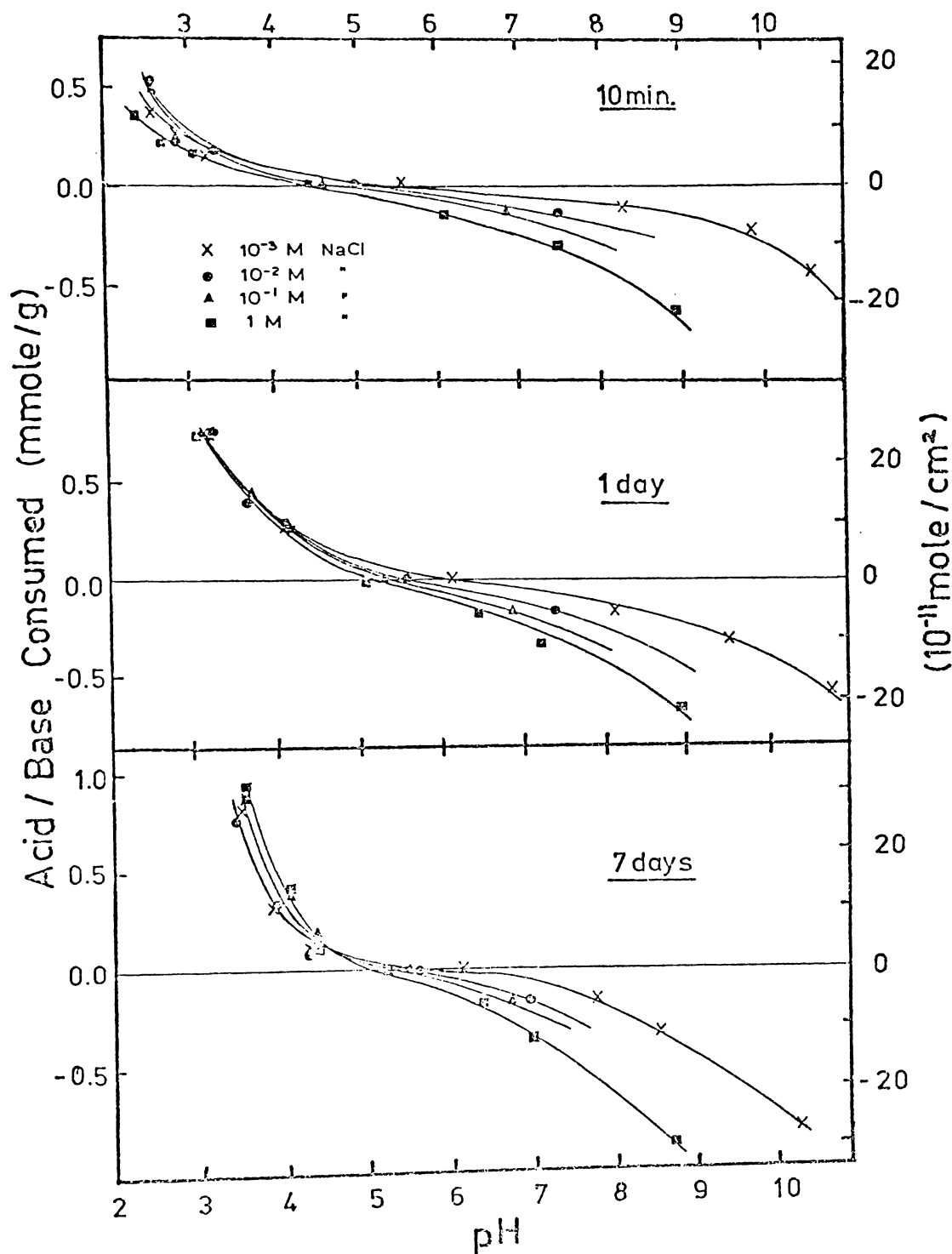


Figure 5.4. Consumption of acid and base by acid-washed Ohaupo allophane after standing for one week as a function of pH and electrolyte concentration at various times of interaction. Clay concentration 2.95 g/l.

octahedral aluminium hydrous oxide as well as a small amount of hydrous iron(III) oxide. The aluminium removed must be considered to have been a part of the surface and not an adsorbed cation in the manner of, say, Ca^{2+} . This is consistent with the concept of the external surface of allophane being at least partly polymeric hydrous aluminium oxide over an aluminosilicate matrix.^{25, 37}

The actual amount of H^+ or OH^- adsorbed ($A \cdot \Delta \Gamma_0^{\pm}$ in (5.1)) is shown in figure 5.5b which includes the correction for aluminium dissolution (Y). All curves tended to be superimposeable on the acid side of the PZC which reflects the greater aluminium concentration found for the stronger electrolyte systems. Bolland et al. found a similar relationship between the concentration of dissolved aluminium and the electrolyte strength.¹³⁵ The cause of the tendency of the apparent surface charge to be independent of the electrolyte (e.g. fig 5.4a+b) concentration is not specific adsorption but may be involved in the mechanism that induced the strong acid ion exchanging behaviour in the freshly acid-washed allophane. Strong acid ion exchangers adsorb H^+ in a more ionic form rather than binding it to weak, not readily dissociated sites to form groups like $=\text{Al} - \text{OH}$ or $-\text{COOH}$.¹⁴⁷ To affect this property the adsorption sites for at least part of the adsorbed acid on the acid-form allophane must be strongly ionic and not dissociated weak acid $\text{Si} - \text{OH}$ or $\text{Al} - \text{OH}$ groups. Allophane, like kaolinite, is considered to have a permanent negative charge in its matrix from the presence of tetrahedral aluminium. These charges must be satisfied at a distance and this is usually done in allophane by octahedral aluminium hydroxide species. Acid washing will remove variable amounts of this material and replace it with H_{aq}^+ , adsorbed hydronium ions. These can be released by ion exchange with cations and this is favoured by high electrolyte concentrations. This ion exchange occurs simultaneously with normal surface adsorption at the

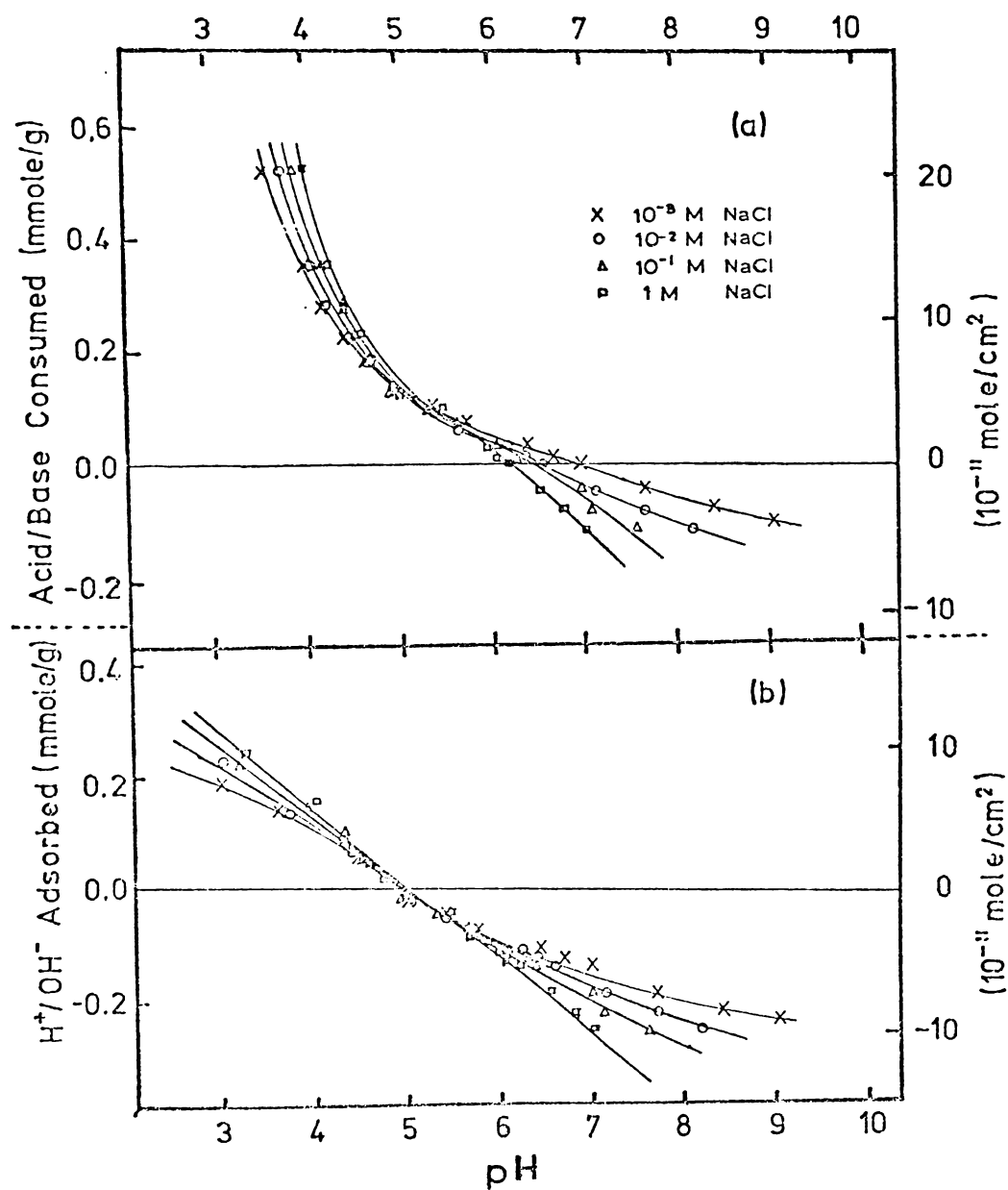


Figure 5.5. (a) Consumption of acid and base by Ohaupo allophane after 24 hours interaction as a function of pH and electrolyte concentration. (b) H^+/OH^- adsorbed by the same suspensions as for (a), i.e., the values have been corrected for by subtraction of the amount of acid consumed by dissolving aluminium.

hydrous oxide hydroxyl groups which adsorb more H^+ as the electrolyte strength grows. The result is an unusual series of close, perhaps collinear, curves.

The ageing process that occurs in acidic media is a slow transfer of aluminium from the matrix to the solution and to permanent charge neutralisation sites otherwise occupied by cations such as H_{aq}^+ or Na^+ , a process well known for hydrogen-form montmorillonite and other acid washed clays.¹⁴⁸⁻¹⁵¹

To investigate further the rôle of acidification upon the surface charge and PZC of aluminous materials a sample of an amorphous aluminosilicate with an Al/Al + Si ratio of 0.556, which is very similar to that of the Ohaupo allophane, was obtained from Dr. K.W. Perrott.* (The preparation of this material is described in reference 77.) The results of the titrations of this material are shown in figure 5.6. The 10 minute acid consumption shows no evidence of specific adsorption and gives an apparent PZC at pH 4.6 which increased on ageing to pH 5.0. Both values are outside the range of IEP's given by Parks¹²⁴ for aluminosilicates of this composition, ~ 5.8, unless there was a large tetrahedral contribution. The figures quoted by Parks were determined by microelectrophoresis and not by ion adsorption, i.e., they were IEP's and not PZC's, and so they are not necessarily completely comparable. (For an alumina a difference of 1.4 pH units was found between the PZC and the IEP,¹⁵² but again the absence of specific effects was not confirmed.) No significant quantity of any specifically adsorbing cation such as calcium was found in the aluminosilicate either chemically or by XRF (section 3.10). Perrott¹²⁵ determined the PZC of this material using Schofield's method with sodium chloride and obtained 6.2, more

*Ruakura Agricultural Research Centre, Hamilton.

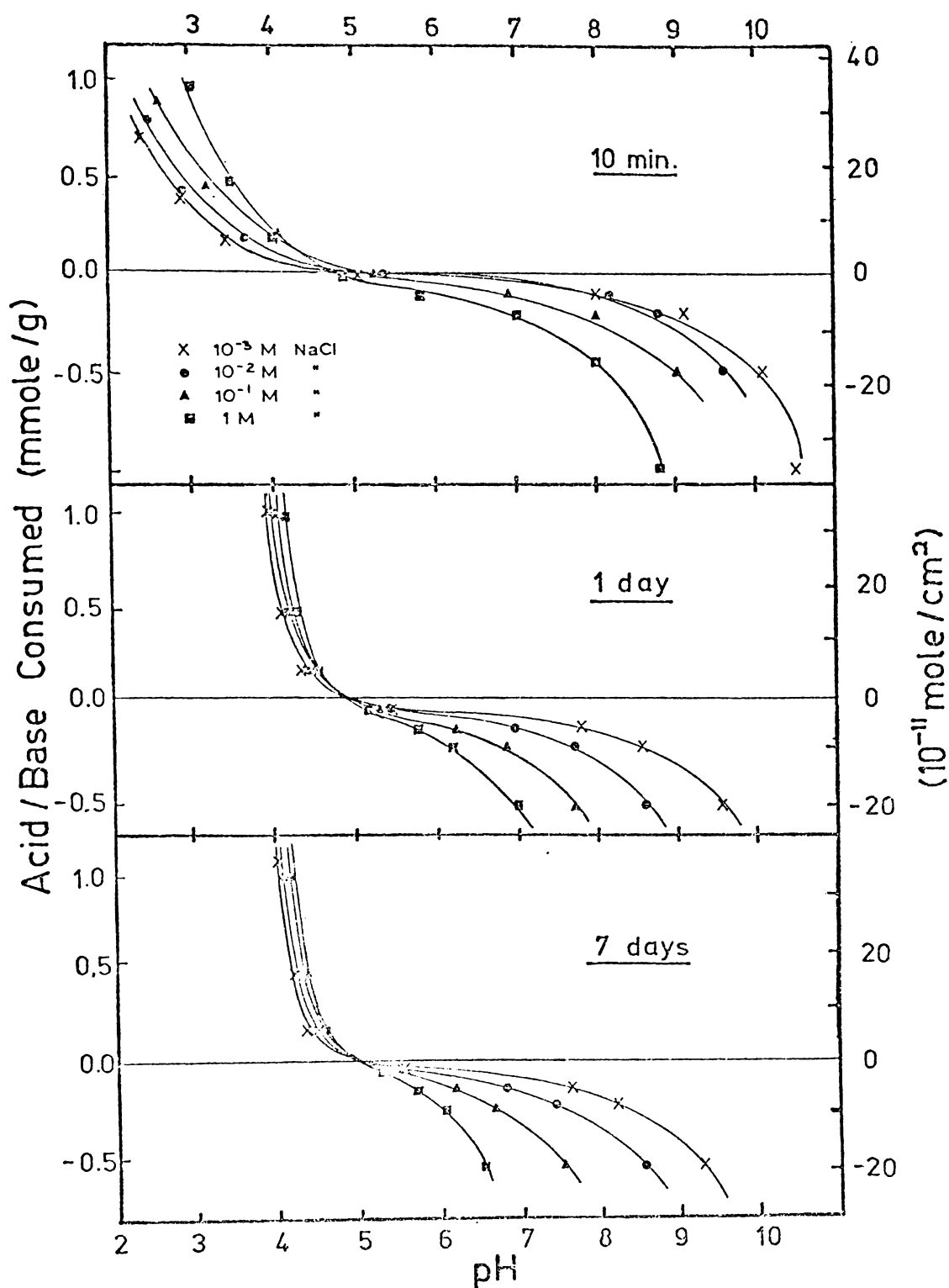


Figure 5.6. Consumption of acid and base by a synthetic aluminosilicate as a function of pH and electrolyte concentration. Aluminosilicate concentration 10 g/l.

than a full pH unit higher than the value determined here. The slopes of the plots near this region (fig. 5.6) are low and only a small contribution to the surface charge from ion-exchange processes rather than adsorption would have a large influence upon the position of the PZC. In fact a change of only 8mmoles/100 g for the 1 M curve would make the point of intersection with the curve of the lowest ionic strength be at pH 6.0; the amounts required for the other curves are somewhat less.

The lack of a definite point of crossover for a material which changes its charge from negative to positive is unusual and has not been observed for similar materials by either Van Raij and Peech¹⁴² or Keng and Uehara¹¹⁷ although a problem of this nature was reported by Espinoza et al.¹⁵³ from their studies of two allophanic soils of Chilean origin. They suggested that the apparent PZC by titration was too low for two reasons. The first was that nitrate adsorption indicated an apparent positive charge at the pH of curve crossover. The second was the difference between this point and the pH of the soil in the salt solution prior to addition of acid or base, the zero point of titration of ZPT. Unfortunately the pH dependent cation adsorption over the same range was not determined and so no point of equivalent ion adsorption was obtained. In addition the ZPT will reflect the state of the soil after its equilibration in the field which will not necessarily be at a pH such that the soil was uncharged. The suggested PZC's between 6 and 7 seem somewhat elevated when compared with the values reported in references 117 and 142 and those determined here.

The influence of permanent negative charge upon titration procedures is again illustrated in figure 5.7, the results for the consumption of acid and base by Mangawara halloysite. After a short time no common point of intersection was observed in the pH region

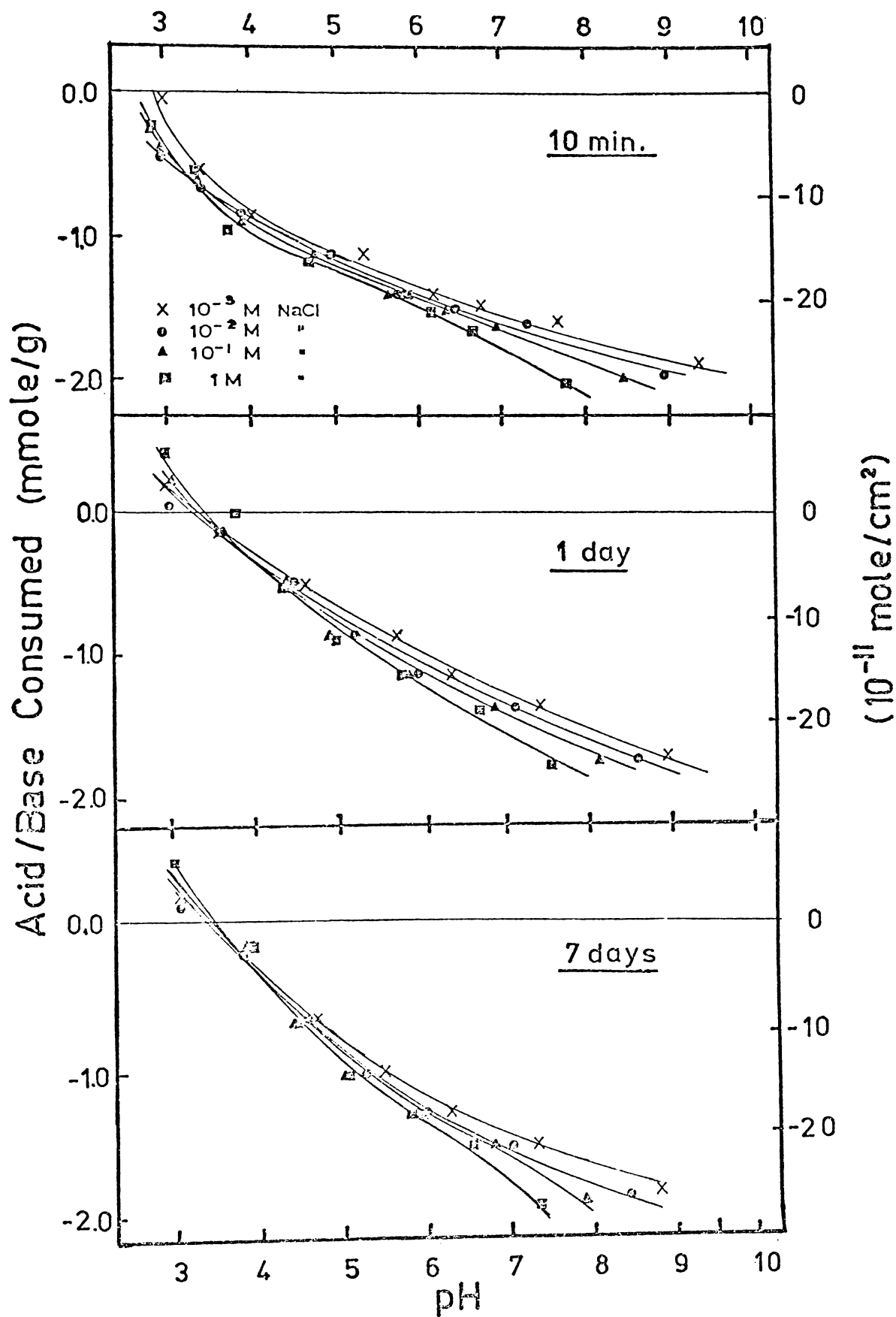


Figure 5.7. Consumption of acid and base by Mangawara clay as a function of pH and electrolyte concentration at various times after interaction. Clay concentration 7.2 g/l.

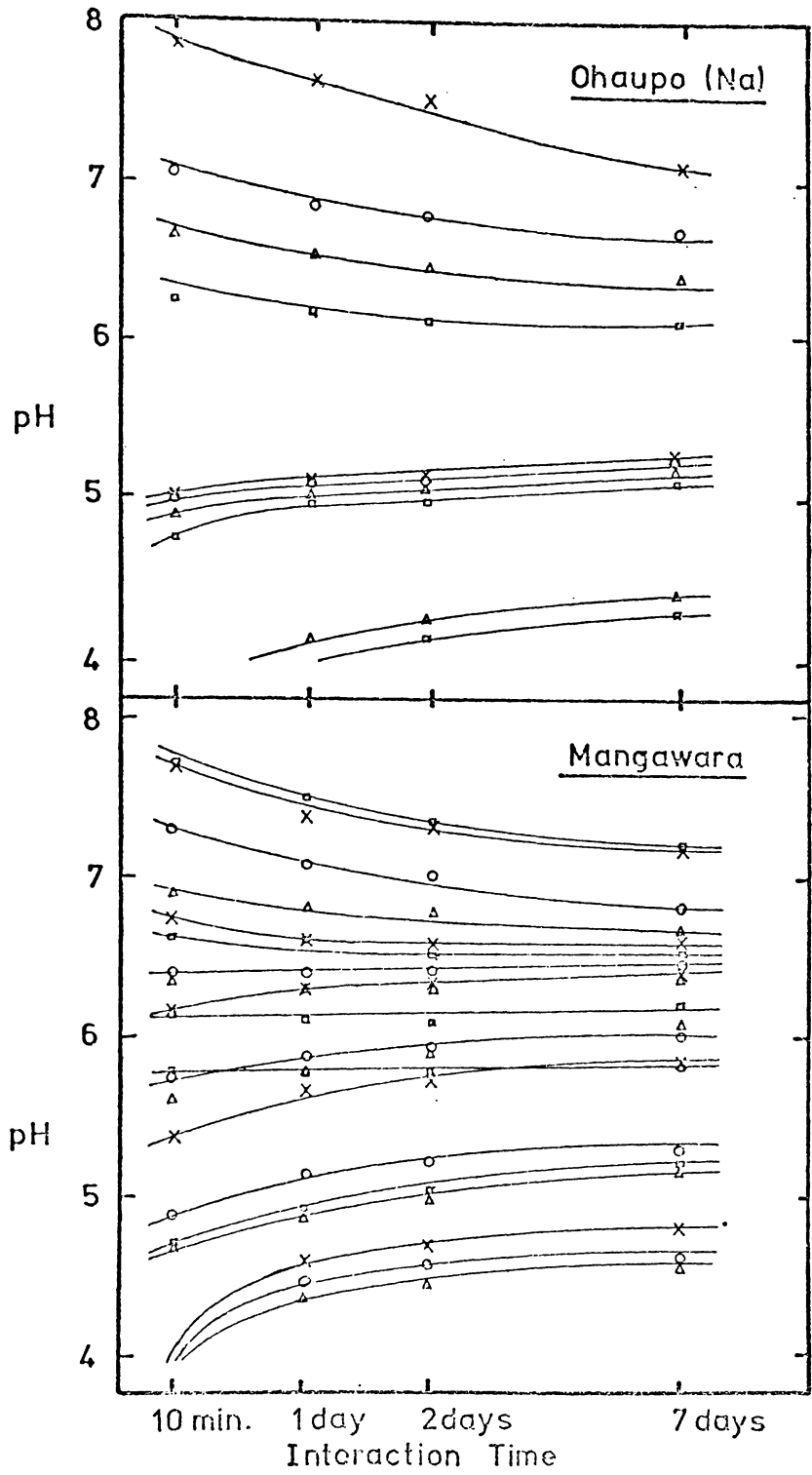


Figure 5.8. Variation of the pH of suspensions of sodium-form Ohaupo allophane and Mangawara clay with time of interaction.

3 to 9 although negative charge appeared to be less well developed at low pH. After some hours an apparent PZC was observed near pH 4 but as surface rearrangements are reasonably rapid this may be expected to be an artifact of aluminium dissolution which is dependent upon the electrolyte concentration. A similar effect was observed by Bolland et al.¹³⁵ for kaolinite. The true PZC of halloysite would then be at low pH like that of kaolinite.

It has been suggested that the pH of a suspended oxide in an electrolyte will tend to move in the direction of its PZC with time.^{106, 154, 155} As the PZC's are close to the points of minimum solubility dissolution effects seem to have little influence on the PZC's of pure oxides determined by this method.¹²⁴ The values obtained in this manner for mixed oxides should be considered with care, as the results for the various materials used in this study indicate. All of them tended to change their pH in the direction of the pH of least solubility of the most labile component, i.e., the aluminium hydroxide near pH 6 (fig. 5.8). However, the true PZC of the halloysite was much less than 6, in fact it was below 3 so that this method of PZC determination is too unreliable for use with mixed systems and probably also for one-component materials where the PZC does not coincide with the pH of minimum solubility.

5.4.5 Conclusion

This work has shown that the surface charge of allophane suspended in neutral and alkaline solutions can be determined by titration methods. The occurrence of permanent negative charge was found to interfere with the determination in acid systems and resulted in values of the surface charge and the PZC that were low compared with those determined by other methods. Furthermore, in acid suspensions, dissolution particularly of the hydrous aluminium oxide, occurred and this also interfered with the measurements.

This could be minimised if the time of contact was short. Alternatively if the amount and nature of the dissolved material could be determined, then the amount of acid consumed by this process could be calculated and allowed for in determining the surface charge.

As the dissolution cannot be measured readily in the single sample titration procedure this method is unsuitable for surface charge determinations of materials with significant quantities of soluble components. Any method which relies upon pH change with time to determine the PZC will also be too unreliable for general use because of interference from dissolution.

The results of this chapter of particular interest are:

- (i) the relatively high value of the PZC of allophane which, together with its amphoteric nature, separates allophane from the other common clay minerals,
- (ii) the importance the presence of hydrous aluminium oxide has upon the surface properties of allophane, and
- (iii) the modifications to the surface interactions with the potential determining ions that occur after acid washing.

The consumption of acid and base by allophane can be understood in the terms of current concepts of its structure (see section 2.4) i.e., by the reactions of its hydrous aluminium oxide or the exposed aluminosilicate core.

CHAPTER SIX

ION ADSORPTION : A REVIEW OF THE LITERATURE

6.1 Introduction

The partitioning of ions between solutions and solid interfaces, and the phenomena which influence this process, is of considerable interest in many disciplines. To the agriculturists the retention, fixation and release of ionic nutrients, trace elements, heavy metals and radionuclides has occasioned much research with clay minerals and hydrous oxides. Environmentalists and ecologists are concerned with the binding of the same materials not only by soils but also by suspended matter in bodies of water. Some engineers are interested in ion adsorption when water containing ionic contaminants requires purification; others modify mineral surfaces by ion adsorption to achieve ore separation by flotation, whilst a further group is interested in the changes brought about by electrolytes in the properties of lubricating drilling muds. These fields and many others are within the domain of the colloid and surface chemist.

With allophane the greatest interest has been in its interactions within the soil. However, it is also washed into lakes and rivers during the course of erosion in many areas; there it may have important consequences upon the availability of nutrients. Furthermore if it is to be used as a flocculant for the treatment of industrial effluents^{156,157} the conditions under which it binds simple ionic species should be understood. The interactions of allophane with anions such as phosphate have been the subject of much study elsewhere (e.g., refs. 158-161). Its interactions with cations in dilute solutions have up till now been neglected. For this reason the emphasis in this study is upon cation adsorption from dilute solution.

As allophane behaves like a constant potential material (i.e., like a hydrous oxide), it is to be expected that its interactions with ionic materials will, in principle, be similar to those of the hydrous oxides. These adsorbents have been studied not only because of their importance in many natural and industrial situations but also, because of their simplicity, they may be useful as model systems for the reactions of the more complex clay minerals. In comparison allophane has an aluminosilicate core of variable composition, coated to differing degrees with hydrous aluminium oxide and with iron(III) hydrous oxides also present. The allophane surface may be a complex mixture of all these components or they may be present as discrete phases.

In this chapter the state of knowledge of the partitioning of cations between solutions and the surfaces of hydrous oxides and clay minerals is critically reviewed. A number of theories of the mechanism of adsorption have been proposed; some of these are discussed. In the next chapter a recent theory describing the interaction of ions at the hydrous oxide/aqueous interface is critically discussed. It is then developed into a theory which will assist explanation of the observations of an experimental study of the adsorption of several simple cations by allophane.

6.2 Ion Adsorption and Cation Exchange Capacity

Ion adsorption at a surface, as discussed in Chapter Four, is the result, at least partly, of an electrostatic attraction. The nature of the electric charge of the surface inducing the adsorptive force has been discussed in sections 4.4 and 5.3. This charge has two origins: it may be structural (and pH independent) or it may be associated with surface oxygen functions such as - (Si) - OH and - (Al) - OH groups. In the latter case it varies with pH becoming more positive as pH decreases and more negative as the pH rises. This will cause the distribution of ions between the surface and the solution to be pH dependent, i.e., the ion adsorption, cation and anion exchange capacities (CEC and AEC respectively) will vary with pH. In general all minerals with surface oxygen functions display pH dependent cation adsorption and cation exchange capacities.

The cation exchange capacity of a soil or a clay mineral is the total quantity of exchangeable cations, such as hydrogen, sodium, potassium, ammonium, magnesium or calcium, that it can retain. It has commonly been measured by saturating a sample with a 1M solution of a salt at a predetermined pH, e.g., sodium acetate at pH 7.0, and then determining the quantity of that cation released (or exchanged) by a 1M solution of a similar salt of a different cation, e.g., ammonium or magnesium acetate.^{162,163} This approach has been criticised as the surface charge for constant potential materials is a function of the electrolyte concentration (see Chapter Five). Soil solutions have an ionic strength of the order of 10^{-3} to 10^{-2} M and so exaggerations of the real ability of the soil to retain cations may have been common.^{164,165} A more reasonable approach is to use solutions of similar strength to those in the soil, i.e., about 10^{-2} M.

Cation adsorption and cation exchange capacity measurements differ in that for the former it is the distribution of ions between

the solution and the surface that is of interest whereas for the latter it is the maximum amount that may be adsorbed.

It was from CEC measurements of some minerals, montmorillonite especially, which were constant in weakly acid systems that led Schofield¹⁶⁶ to postulate the existence of permanent negative charge from structural substitution. This charge dominates the electrochemistry of such minerals, which have silica surfaces, when the surfaces are not involved in reactions with the potential determining ions, H^+ or OH^- , i.e., below about pH 5.5. Materials with hydroxylic surfaces, such as kaolinite, allophane and the hydrous oxides, whilst possibly having permanent charge, have surface charges which increase continuously with pH and so their interactions with ions also change monotonically with pH.

The CEC of any mineral sample will also be dependent upon the number of hydroxyl groups, and their acidity, so that clays with a large surface area will tend to have high exchange capacities. Finely divided clays such as allophane and imogolite, which have large surface areas and high concentrations of surface hydroxyl groups, also have large cation exchange capacities. For a wide range of minerals Sawhney and Norrish¹⁶⁷ observed a near linear relationship between CEC at pH 8.2 and surface area, as measured by the adsorption of nitrogen, which was said to relate the CEC to the concentration of surface hydroxyl groups.

6.3 Ion Adsorption by Hydrous Metal Oxides

6.3.1 Alkali Metal Cations

Adsorption of simple monovalent cations of the alkali metals onto hydrous aluminium oxides from dilute aqueous solutions is strongly pH dependent¹⁶⁸ and does not occur with any strength below the point of zero charge (PZC).¹⁶⁹ Similarly none of these cations sorbs strongly

onto haematite below its PZC^{116,170,171} except for lithium from high concentrations which, because of its similar ionic radius, may replace an iron(III) ion in the oxide matrix.^{116,171} At moderate surface charges there is no specific interactions between these cations and hydrous iron(III) oxides^{171,172} or with silica gel,¹⁷³⁻¹⁷⁶ and adsorption follows the lyotropic series. This is the order of selectivity shown by ion exchange systems for cations in the absence of specific chemical interactions, i.e., ϕ^+ of equation (4.28) tends to zero. As the strength of binding of a mobile ion is purely electrostatic it will depend upon the ion charge and its distance of separation from the surface. In aqueous systems most ions are hydrated with a strength that is inversely related to the Pauling ionic radius so that small ions are more strongly hydrated and consequently their effective size is actually greater than the less hydrated larger ions. The larger and more polarisable ions may easily part with their hydration sheath and allow closer approach to an adsorption site.¹⁴⁷ For monovalent cations this series of ease of adsorption is (most strongly bound first): $\text{Tl}^+ > \text{Ag}^+ > \text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Li}^+$.

At very high electric field strength, i.e., at high surface charge densities, near pH 12 the reverse order for the alkali metal cations, $\text{Li}^+ > \text{Na}^+ > \text{K}^+ \sim \text{Cs}^+$, has been observed for haematite.¹⁷² This has been explained in terms of the structured water model which proposes considerable fixed orientation of the water occurs at surfaces which have high electrostatic fields.¹⁰⁶ On ion hydration the binding energy of the water molecule is partly compensated by a loss in its entropy as it becomes restricted in its movements. If the water in a region is already structured the loss of entropy from cation adsorption will be lower and so the cation with the greatest order in its hydration sheath will apparently be preferentially adsorbed. A similar reversal of preference has been recorded for similar circumstances with

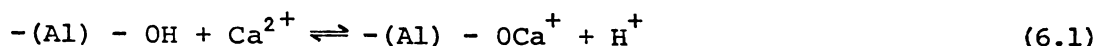
hydrogen and aluminium form silica gel at high pH and also with sodium and calcium form gel at lower pH.¹⁷⁷ In all cases the surface was highly charged. The preference order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ \sim \text{Cs}^+$ is the same as the order of stability of the hydroxyl complexes.¹⁴⁶ It was suggested that some degree of covalent bond formation with the surface was occurring.¹⁷⁷

Thallium(I) behaves very much like potassium or rubidium in its interactions with ion exchange materials.¹⁶⁸ This is also true of its interactions with hydrous iron(III) and manganese(IV) oxides.¹⁷⁸ The adsorption increased with pH from near zero at the PZC of the adsorbent. At low pH in the manganese(IV) system the thallium(I) was oxidised to thallium(III) which adsorbed much more strongly and made the isotherm appear anomalous.

6.3.2 Multivalent Cations and the Rôle of Hydrolysis

As a consequence of their greater charge multivalent cations are usually sorbed more strongly than monovalent cations. In the absence of hydrolysis adsorption tends to follow the lyotropic series. At pH 2 the following series has been observed on silica¹⁷⁶: $\text{Ba}^{2+} \gg \text{Hg}^{2+} > \text{Fe}^{3+} > \text{Pb}^{2+} > \text{Sr}^{2+} > \text{Cd}^{2+} > \text{Al}^{3+} > \text{Ni}^{2+} > \text{Sn}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Co}^{2+} > \text{Ag}^+ > \text{K}^+ > \text{Na}^+ > \text{Mg}^{2+}$. A similar sequence was observed for cation adsorption by a hydrous iron(III) oxide except that at high concentrations magnesium, like lithium, is particularly strongly adsorbed.¹⁷¹ At the same time adsorption of multivalent cations tends to increase with pH from well below the PZC, i.e., in (4.28) most multivalent ions have non-zero ϕ^+ and are said to specifically adsorbed.^{171,179,180} Many anomalies can be found in the preferences surfaces show for ions. Quartz and iron(III) hydrous oxides follow the order $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ at high and low pH¹⁷⁹⁻¹⁸¹ but alumina has the opposite preference.^{179,182} Adsorption of Ca^{2+}

appeared to correlate with the release of one proton.^{179,182} (The method used to obtain this figure is criticised in the next chapter.) The following exchange was postulated;



The nature of the surface complex $-(Al) - OCa^+$ was not specified except that the calcium ion was said to be specifically adsorbed. The structured water model was invoked to explain the adsorption sequence as the pH for some adsorption appeared too low to allow significant hydrolysis, necessary to allow formation of a covalently bound complex.

In the pH region where a cation may hydrolyse its adsorption invariably increases greatly. On aluminium hydroxide the preference follows approximately the stability of the first hydrolysis complex MOH^{Z-1} , (Table 6.1), when coupled with selection for small ions;¹⁸² $Cu^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$, whilst similar sequences with selection for large ions have been observed for hydrous iron(III) oxides; $Pb^{2+} > Cd^{2+} > Zn^{2+} > Ca^{2+}$;^{178,184} $Hg^{2+} > Cu^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+}$;¹⁸⁵ and $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+} > Co^{2+} > Sr^{2+} > Mg^{2+}$.¹⁸² At increased pH silica adsorption sequences show a greater dependence upon hydrolysis than upon ion size; $Al^{3+} \sim Fe^{3+} \sim Cr^{3+} > Co^{2+} \sim Cu^{2+} > Zn^{2+} > Ba^{2+} \sim Sr^{2+} > Ca^{2+} \sim Mg^{2+} > Rb^+ \sim K^+ > Na^+$ at near neutral pH^{173,186,187}

Dugger *et al.*¹⁷³ and Wakatsuki *et al.*¹⁸⁷ both proposed mechanisms similar to (6.1) but with the possibility of more than one silanol group (for silica) being involved with a cation. Some similarities might be expected before the reactions of OH^- and $-(Si) - O^-$ towards metal ions. Hydrolysable ions may enter into complex formation with silanol groups and the surface may then act as a multidentate ligand. The metal ion-surface bond might also involve hydrogen bonding in the following manner which releases H^+ ;

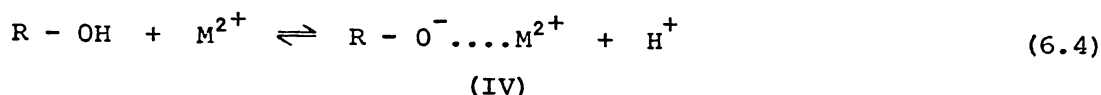
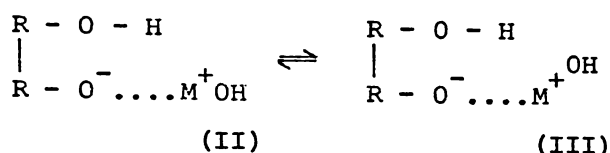
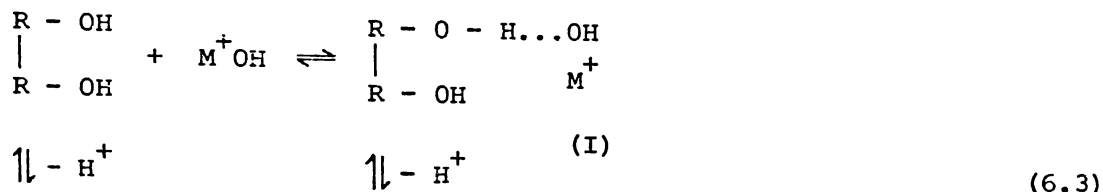
Table 6.1 Ionic Radii and Stability Constants for the First Hydroxide Complex of some Divalent Cations

Cation	Pauling radius(1) 10^{-10} m	$\log K_1$ (2)
Mg	0.65	2.58
Ca	0.99	1.3
Sr	1.13	0.85
Ba	1.35	0.68
Mn	0.80	3.3
Fe	0.75	3.9
Co	0.72	2.8
Ni	0.69	3.1
Cu	0.92^g	6.7
Zn	0.74	5.0
Cd	0.97	6.1
Hg	1.10	10.3
Pb	1.27	7.82

(1) from ref. 183.

(2) from ref. 146; $K_1 = [\text{MOH}^+]/[\text{M}^{2+}][\text{OH}^-]$.

g Goldschmidt radius from ref. 183.



Apparently adsorption of calcium onto hydrous iron(III) oxide could be consistent with either (I) or (IV)¹⁸⁰ whilst adsorption of more strongly hydrolysing ions, which appeared to release more than one proton per ion sorbed,¹⁸² could also involve species (II) and (III) as well. The nature of the surface hydroxyl-metal ion interaction for (II) and (III) has not been specified. Direct bonding and association of the fully hydrated cation with the surface have been suggested as the modes of interaction for the sorption of lead onto hydrous iron(III) oxide because of its readiness for replacement (fully hydrated cation) in some situations and difficulty (direct bonding) in others.¹⁸⁸

Forbes et al.¹⁸⁹ measured the amount of acid released by the adsorption of divalent cations on goethite and found a near stoichiometric exchange, i.e., about two H^+ per cation. Similar stoichiometric exchanges have been found for cation adsorption by silica.^{173, 190, 191} Although with goethite a value other than two was not ruled out¹⁹² the species (I) and (IV) of the above reaction scheme would seem unlikely. So too does the hydrolysis reaction (6.2) or, in fact, any other adsorption process that invokes hydrolysis in a

suspension of pH where only a very small part of the free cation can be involved in hydroxy-complex formation. The mechanism of cation adsorption, an ion exchange process, is discussed further in Chapter Seven.

6.3.3 Rôle of the Dielectric Constant of the Adsorbent in Cation Adsorption

An observation not yet considered is that at the silica surface adsorption of Co^{2+} and Ca^{2+} increases profoundly in the region of hydrolysis of each, at pH 6 to 7 and 9 to 10 respectively, whereas at the rutile (TiO_2)/aqueous interface both cations adsorb strongly in the same low pH region.¹⁰² A major part of this difference may be associated with the dielectric constant of the substrate which strongly influences energy changes. James and Healy¹⁰⁴ have suggested that cations adsorbed onto silica surfaces, especially when they may hydrolyse, are separated from the surface of the solid by one water molecule. Some of the evidence cited to support this theory, such as that referring to the hydration status of ions on exchange resins, may be reasonable although resins are strong acid systems and oxides are comparatively weak; other interpretations are questionable. From their own work and that of Hahn and Stumm¹⁹³ they found that the maximum adsorption density for cobalt and aluminium sorbed onto silica corresponded to a monolayer coverage of species radius $r_i + 2r_w$ where r_i is the Pauling ionic radius and r_w is the radius of a water molecule. Although this indicates at least part of the solvation sphere is retained the apparent radius is only a measure of the surface area occupied by each sorbed ion and not the distance the ion is from the surface. (At elevated temperatures even some of this water can be lost.¹⁹⁴) It was suggested that the studies of Hathaway and Lewis¹⁹⁵ indicated that on adsorption at the silica/aqueous interface there was

little perturbation of the primary hydration sphere of a potentially hydrolysable cation. However, the spectral data presented was inconclusive as to the nature of the coordinated groups and coordination of free silicate was actually proposed.¹⁹⁵

Notwithstanding the above, with a system of low dielectric constant such as silica ($\epsilon_0 = 4$ to 5^{196}) the energy of adsorption of an ion requiring some loss of its primary hydration sheath is apparently inconsistent with experimental results.^{102, 104} Bolt¹⁹⁷ pointed out that short range interaction between ions and surfaces can only be appreciable if dehydration of the ion close to the surface occurred and he further stated "in the case of cations and counterions dehydration does not seem probable, in general, unless the dielectric constant of the colloid exceeds that of water." Thus short range interaction of divalent ions and silica would not be strong. Rutile, haematite and corundum all have somewhat higher dielectric constants than silica (170, 25, 12 and 4 respectively^{51, 196}). Hydration of a surface usually increases the values of these constants towards that of water¹⁹⁸ (80 at 20°C). Thus adsorption of multivalent ions will be more facile on these surfaces than onto silica and dehydration will be less important. This has been shown clearly by James and Healy¹⁰² for cobalt adsorption onto both rutile and silica. For rutile adsorption occurred at a lower pH, and was mostly of the divalent species, than on silica even though rutile has a much higher PZC. Hydration of the cation is apparently such a hindrance to adsorption onto silica that hydrolysis is needed to reduce the solvation energies enough to allow significant adsorption to proceed.

6.3.4 Maximum Adsorption Density

A further phenomenon that has been observed is the increase in the apparent maximum cation adsorption capacity of a hydrous oxide

surface with pH.^{110,179} For a surface with a limited number of adsorption sites if only a monolayer of adsorbate may occupy these sites then the concentration dependent adsorption isotherm takes the form of the Langmuir equation;

$$\frac{c_s}{x} = \frac{c_s}{x_{\max}} + \frac{1}{\alpha x_{\max}} \quad (6.5)$$

where c_s is the equilibrium solution concentration, x is the amount of adsorbate per unit area of adsorbent, $x_{\max}$ is the amount of adsorbate required to form a complete monolayer and α is the adsorption intensity, a term related to the strength of the adsorption. A plot of c_s/x against c_s should be linear with slope $x_{\max}$. (6.5) can be rearranged as;

$$x = \frac{x_{\max} \cdot \alpha \cdot c_s}{1 + \alpha c_s} \quad (6.6)$$

which is similar to the Stern equation (4.28) if x is identified with σ_i/ze , $x_{\max}$ with N_1 , c_s with c_s/M_h and α with the exponential function. Langmuir-type plots have been obtained for calcium adsorption onto hydrous alumina¹⁷⁹ and zinc onto goethite.¹¹⁰ In each case the apparent maximum surface concentration increased dramatically with pH as shown in figure 6.1a. The logarithm of the maximum adsorption density, $\log x_{\max}$, was taken from figure 4B of reference 179; it clearly increases linearly with pH (fig.6.1b).

The hydrous oxide surface has then a maximum capacity which is dependent upon the pH. It is also dependent upon the nature of the cation; those ions which bind more strongly also bind to a greater extent at a constant pH. This has been found for manganese(IV) oxide where the maximum capacity for cobalt, which sorbs most strongly, is greater than for zinc which in turn is greater than for calcium, the least firmly bound.¹⁹⁹

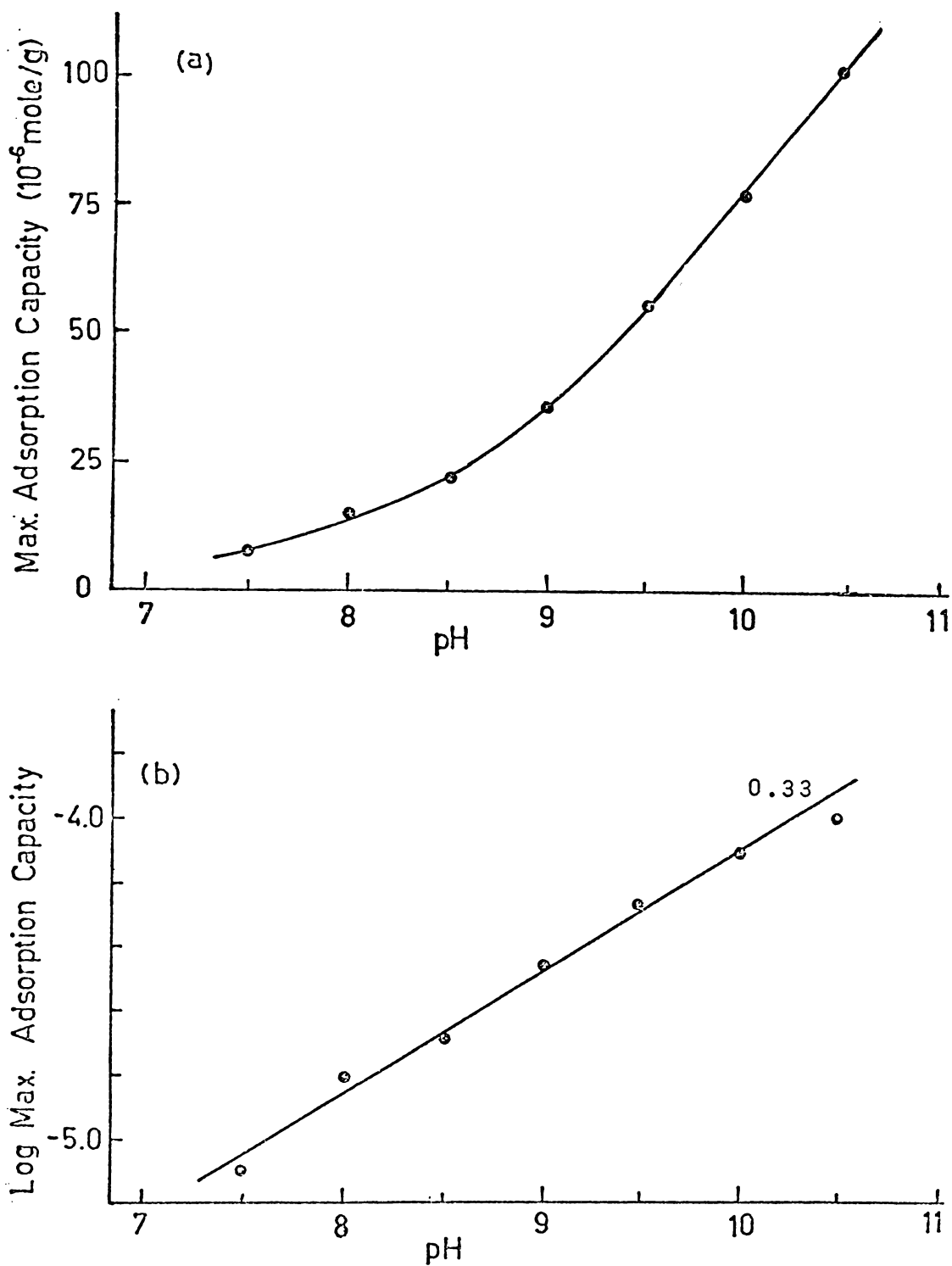


Figure 6.1. Adsorption of calcium by alumina (redrawn from ref. 179). (a) Maximum adsorption capacity, (b) logarithm of the maximum adsorption capacity.

6.3.5 Adsorption of Anions

The adsorption of anions by hydrous metal oxides has a number of similarities to cation adsorption. The major difference is that the pH effect is reversed, i.e., adsorption decreases as the pH rises. The adsorption preference sequence shows dependence upon similar ion characteristics and the most strongly adsorbed species are those which are highly charged and hydrolysable. A typical sequence for anions adsorbing onto iron(III) hydroxide is (as their neutral acids); $\text{H}_3\text{AsO}_4 > \text{HVO}_3 > \text{H}_3\text{PO}_4 > \text{H}_2\text{MoO}_4 \sim \text{H}_4\text{SiO}_4 > \text{H}_2\text{SeO}_4 > \text{H}_3\text{BO}_3 \sim \text{H}_2\text{SO}_4 > \text{HCl} \sim \text{HNO}_3$.¹⁸⁷ Non-specifically adsorbing monovalent anions such as chloride and nitrate do not adsorb strongly above the PZC but other multivalent anions such as sulphate and phosphate do. These higher charged ions can shift the apparent PZC to higher pH; the reverse of the change caused by multivalent cations.

There are two main mechanisms of anion adsorption. It may proceed following surface protonation in which case the anion remains as a surface counterion to a positively charged surface group. Anions such as nitrate, chloride and sulphate bind to oxides such as rutile,²⁰⁰ alumina,¹⁶⁹ goethite,²⁰¹ chromium(III) oxide²⁰¹ and haematite¹⁷¹ by this manner. Alternatively the adsorption may be by exchange for surface groups (c.f. the adsorption of hydrolysed cations) in which case the anion becomes covalently bound to the matrix metal cation. In some cases at high activity, with phosphate at least,¹⁷¹ the anion may become potential determining, i.e., the surface has taken on the characteristics of the metal phosphate at the expense of the hydroxide. Systems that show ligand exchange of this nature include fluoride, selenite and phosphate adsorbing onto goethite,^{133,202,203} and phosphate on goethite,²⁰¹ haematite¹⁷¹ and alumina.²⁰⁴

Maxima in the adsorptions of anions occur at $\text{pH} = \text{pK}$. This has been taken to show the necessity of having both proton donors and

proton acceptors present to enhance adsorption, the neutral acids are not strongly adsorbed;^{133,202} e.g., the major adsorbing species of orthophosphate are H_2PO_4^- and HPO_4^{2-} .²⁰⁵

A difference between the adsorption characteristics of hydrolysable cations and anions at the hydrous oxide surface becomes evident at this point. Adsorption of cations is strong even when they are sufficiently hydrolysed to form neutral hydroxides but neutral acids tend to remain in solution. This might be correlated with their general aqueous solubilities; many acids are liquids and are miscible with water but the hydroxides of readily hydrolysable metals form separate phases.

6.3.6 Influence of Anions on Cation Adsorption

The presence of anions can influence the adsorption of cations by hydrous oxides in three ways.

First, the hydroxide ion can enhance adsorption by increasing the surface negative charge and by hydrolysing the cation; these effects have been discussed previously.

Secondly, anions may interfere by forming stable complexes with the cation. These complexes may not be readily bound. A particular case occurs with the adsorption of mercury(II) by both silica²⁰⁵ and goethite¹⁸⁴ from solutions containing chloride. Mercury(II) is probably bound to silica and goethite by a hydroxo bridge¹⁸⁴ and this is stable only if the pH is sufficiently high to ensure hydrolysis to $\text{Hg}(\text{OH})_2$. In the presence of chloride the non-adsorbing chloride complex, HgCl_2 , is formed. The mercury then remains in solution unless the pH is very high in which case hydroxy-chloro complexes of Hg(II), capable of binding through the hydroxide ligand, can form.

The third influence arises when anions are specifically adsorbed. This will increase the surface negative charge, as seen from the

diffuse layer, and so enhance the adsorption of cations. Specific adsorption of anions such as selenite, phosphate, arsenate and sulphate onto hydrous oxides has been reported, but the influence of this phenomenon upon cation adsorption was not described. This process has been investigated for soil constituents and phosphate, pyrophosphate and oxalate all greatly increase the CEC of not only the clay fractions of a wide variety of soils but also of some synthetic aluminosilicates.¹³⁸ The adsorption of zinc by plants from soils containing hydrous iron(III) oxides was prevented by the addition of phosphate to the soil.²⁰⁷ Presumably the phosphate was adsorbed by the hydrous oxide and this in turn firmly bound the zinc.

6.3.7 Summary of Cation Adsorption by Hydrous Oxides

Two phenomena promote cation adsorption by hydrous oxides from aqueous solution. These are electrostatic attraction and bond formation. Both are modified by the following properties of the surface and the ion itself:

- (i) the surface charge which is a function of the p.d. ion concentration, i.e., pH. Adsorption generally increases with pH.
- (ii) the charge and ionic radius of the cation. Adsorption tends to increase with cation size and charge.
- (iii) the state of hydrolysis of the cation, another function of pH. Upon the onset of hydrolysis adsorption is greatly enhanced.
- (iv) the surface dielectric properties.
- (v) the nature of other adsorbed species (including surface hydration and the presence of surface charge modifying groups).
- (vi) the occurrence of other specific effects such as inclusion,

complex formation and redox influences.

6.4 Ion Adsorption by Clay Minerals

6.4.1 Effects of the Mineral

Because of the presence of more than one ionisable species and charge site, variations in the sorptive characteristics of clays are not as regular as those of the hydrous oxides. Montmorillonite, for example, has a high permanent negative charge from isomorphous substitution and only a small pH dependent charge so that in the pH region 4 to 8 its cation adsorption properties are almost pH independent in the absence of hydrolysis.^{127, 137, 208} Outside this range protonation and dissociation or hydroxylation, have strong effects²⁰⁹ and the plot of ion uptake against pH has two points of inflexion.²¹⁰ This contrasts with adsorption on most other clay minerals where the ion uptake varies monotonically with pH, e.g., sodium adsorption by kaolinite.²¹¹ Sorption onto kaolinite is similar to that onto silica at low and neutral pH but at high pH for cations it is enhanced by the aluminous groups which become negatively charged. The likelihood of kaolinite having at least two surface components has support from the electrophoretic studies of Buchanan and Oppenheim;¹³² they suggest that its surface chemistry should be considered in terms of silanol or aluminium hydroxyl species depending upon the pH. When freed of surface aluminium kaolinite, montmorillonite and vermiculite all lost pH dependent alkali metal cation adsorption characteristics in the near neutral pH range; in such materials the pH variable properties arise from the surfacial hydroxylic components.

The nature of the clay mineral has a strong bearing upon the influence of concentration on cation adsorption. A correlation may be observed between pH dependent and concentration dependent adsorption, within reasonable limits.

This arises because a surface whose reactivity varies with the activities of one ionic species (e.g., H^+) will also respond to changes in the activities of other ions. The CEC of montmorillonite is independent of both pH (between 4 and 8) and cation concentration whilst halloysite, kaolinite, allophane and imogolite, like the hydrous metal oxides, respond to changes in both (see figs. 6.2a and b).

6.4.2 Influences of the Cation

In general the preferred sequence for alkali metal cation sorption follows the lyotropic series, i.e., $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$, (refs. 45, 127, 164, 211-215). In some cases the adsorption of one ion is greatly increased and fixation may occur particularly with the layer minerals. The ions K^+ , Rb^+ , Cs^+ and NH_4^+ lose their hydration shells on entering the space between the negatively charged layers which then meet the ion solvation requirements; other ions such as Mg^{2+} , Ca^{2+} , and Na^+ are adsorbed hydrated. (A review of this subject is given by Sawhney.²¹⁶) Divalent ion adsorption sequences generally also follow the lyotropic series (refs. 127, 207, 217-219). Size effects can be sufficiently important to cause magnesium to be sorbed more weakly than rubidium.²²⁰ Two major exceptions to this order occur. Vermiculite sorbs magnesium particularly strongly between its highly charged silicate layers which induce strong field effects.^{217,221,222} At increased pH, especially for montmorillonite, the alkaline earth metal cation sequence is approximately reversed from its lower pH order, an effect that has been correlated with ease of hydrolysis and hydroxide precipitation.^{210,223} Chaussidon²⁰⁹ found that the ionic behaviour appeared monovalent at elevated pH and corresponded to MOH^+ , the suggested adsorbing species.^{210,223}

Hodgson^{224,225} showed hydrolysis of transition metals was important in specific adsorption and that surface hydroxyl groups were

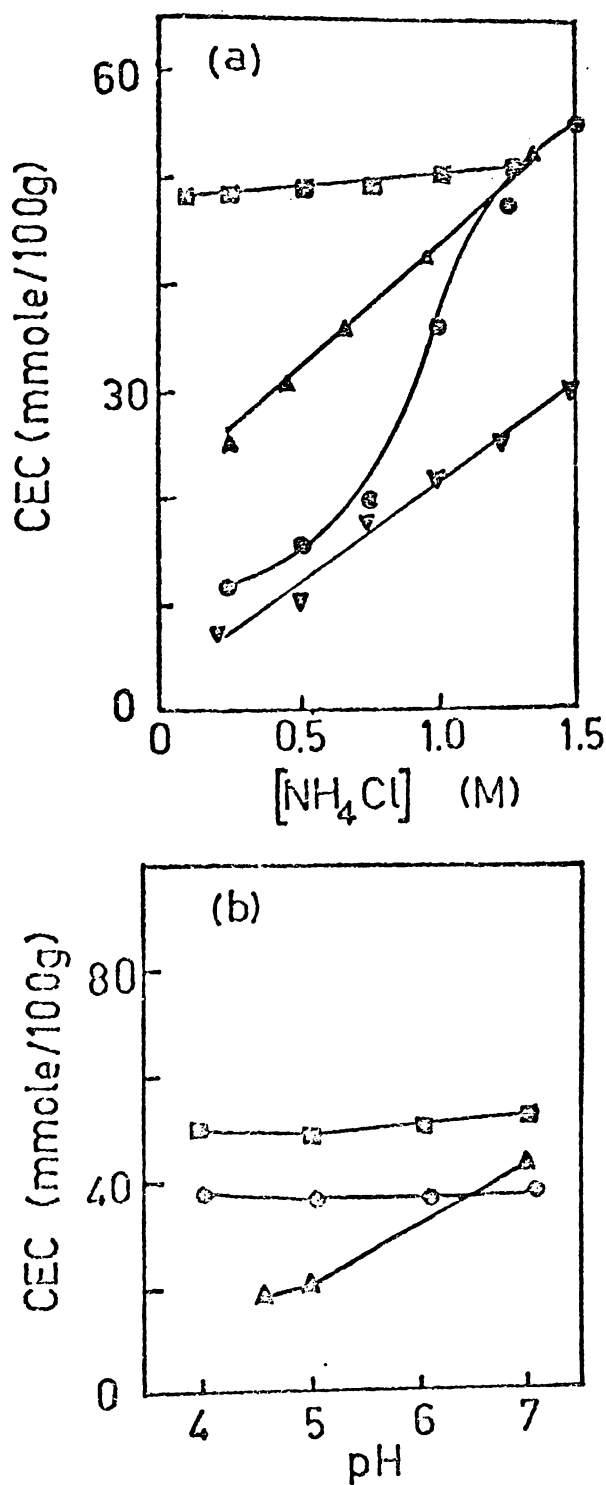


Figure 6.2. Variation of the CEC's of several clays with (a) concentration of the determining salt and (b) pH.

● halloysite; ■ montmorillonite;
 ▼ allophane (pH 5.0); ▲ allophane (pH 7.0). (Redrawn from ref. 137.)

involved even on high permanent charge montmorillonite.²¹² The general selectivity orders are, as with the hydrous oxides, a combination of hydrolysis and hydration strengths (or ion size): $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mn}^{2+} > \text{Mg}^{2+}$ ^{207,218,224,226} and $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+} \sim \text{Ni}^{2+} \sim \text{Mn}^{2+}$.^{224,227} Exchange and infrared spectral data also showed direct involvement of the surface hydroxyl groups of montmorillonite, illite and kaolinite in lead adsorption;¹⁸⁸ at pH < 6 the hydrated ion was the major adsorbed species but increasing the pH decreased the amount of exchangeable lead and increased the proportion chelated to the surface.

At high pH it has been suggested that the kaolinite surface can act as a nucleation centre for hydroxide precipitation, particularly with copper.²²⁸ Because adsorption appeared at lower pH than precipitation it was also suggested that the hydroxide ion concentration close to the surface was greater than in the bulk. However near a negatively charged surface, such as that of kaolinite at neutral pH, the concentration, and hence the activity, of anions such as hydroxide is reduced (section 4.8.4) and so this explanation for the adsorption is erroneous. Furthermore these authors suggested that copper adsorption might proceed not only upon the negative surface but also by hydroxide adsorption onto positive edge charges with subsequent copper deposition. Electron spin resonance spectroscopy has since shown that these edge hydroxyls were of little importance for copper adsorption and the cation was evenly distributed across the planar surface.²²⁹ This is consistent with the negative charge being associated with the silica layer. Nevertheless, it was shown that where ligands capable of forming stable complexes able to maintain copper in solution at high pH could form adsorption onto clay minerals was substantially reduced and did not proceed at all if the complex was neutral or negatively charged.²²⁸

The exchange of copper and calcium cations on kaolinite was studied by Kishk and Hassan²³⁰ at pH 3.3 where calcium was preferred, and at pH 5.2 where copper was preferred. This behaviour, which is similar to that reported by El Sayed et al.,²³¹ was related to the competition of H^+ with Cu^{2+} . This was said to be more effective at lower pH than at high.

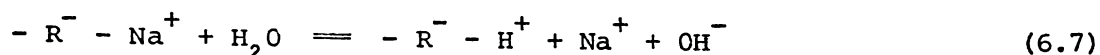
Trivalent ions usually adsorb to a greater extent than the lesser charged species.^{197,208,219} These ions have very large influences upon the surface properties; as they hydrolyse strongly they may completely coat the clay and force it to act like a particle of the precipitated hydroxide.^{131,232}

The cation effects on adsorption at clay surfaces are similar to those at the hydrous oxide surface. In general selectivity follows the lyotropic series with allowance for hydrolysis which suggests a low dielectric constant such as observed for silica. The ready adsorption of cations in the divalent state however suggests a higher dielectric constant. This concurs with the determinations of this property for the aluminosilicates which have shown it to be intermediate between quartz and corundum.⁵¹

6.4.3 Effect of Acid Treatment on Cation Adsorption

Washing soils and clays with distilled water or dilute mineral acid is frequently carried out to remove readily exchangeable ionic species and reduce surface salt concentrations. (Leaching of hydrous metal oxides has little permanent effect as dissolution of the surface layer exposes a material which will assume the same characteristics.²⁰⁰) With minerals of mixed composition quite dramatic irreversible effects can be produced.

Washing clays with distilled water can remove bound ions by a hydrolysis or exchange reaction;



A comparable reaction may proceed for the hydrolytic loss of anions. In some cases the adsorbed proton may then attack the structure and release aluminium (or magnesium from the magnesium based clay minerals) which can then assume the surface adsorption site.^{151, 233} Water can also dissolve finite quantities of the minerals particularly as aluminium and silicon hydroxides are both slightly water soluble.^{234, 235} This process also alters the surface properties. Silicon hydroxide is more soluble than aluminium hydroxide at pH 6 so leaching at this pH results in a more aluminous material with a more positive surface charge.¹³² Acid treatment, on the other hand, removes the more acid soluble fractions, such as the divalent cations¹²⁷ and aluminous materials, which results in a more siliceous surface with an intensified negative charge.¹³² If the acid strength and quantity are great enough silica gel may form following dissolution of the acid soluble materials from some clay minerals.²³⁶

Addition of aluminium to clay and soil surfaces usually results in large decreases in their CEC's^{150, 237} because the aluminium occupies adsorption sites and, as its hydrous oxide has a high PZC, in the hydrolysed form it will not adsorb cations readily. Subjecting soils²³⁸ and clays²³⁹ to processes which remove their iron(III) was found to increase their CEC and ability to adsorb cobalt(II). As the reagents used also remove aluminium it may not be stated unequivocally that it was the loss of iron that brought about the change; it may also have been the aluminium loss. However, acid washing of montmorillonite impaired its ability to adsorb cobalt from a dilute solution of 0.05M calcium chloride.²²⁴ The mechanism was not known but it may have involved the transport of aluminium from the matrix to adsorption sites. Although this result is quite different from the usual immediate result

of acid washing of the lower crystalline clay minerals it is the same as that observed in this study for the ageing of allophane and halloysite in acid (see Chapters Five and Nine).

6.4.4 Adsorption of Cations by Allophane

The adsorption of cations by allophane from dilute solution has not previously been reported although Fieldes and Schofield³⁰ measured sodium retained by some allophanic clays from 0.2M sodium chloride. They found the adsorption increased slowly with pH between pH 4 and 5 and more rapidly above pH 6. The cation exchange capacity has been more frequently studied and it has been found to increase with pH and concentration, charge, and ionic radius of the determining cation (refs. 20, 31, 137, 240-243).

The ability of allophane to bind cations has been attributed to its permanent negative charge from structural isomorphous replacement (section 2.4) but this may be blocked by adsorbed aluminous groups.²⁴⁴ With pH increase it has been suggested that the aluminous groups become deprotonated and less able to neutralise the structural charge, consequently increasing the CEC.²⁴⁴⁻²⁴⁶ Alternatively the variable charge might arise from the presence of aluminium in tetrahedral coordination, linked by hydroxyls. This coordination would give these hydroxyls weakly acidic properties and they would ionise to a pH dependent extent, providing negatively charged cation retention sites.²⁴⁷ The possibility that the dissociating groups are silanolic hydroxyls influenced by the tetrahedral aluminium of the core has also been raised.²⁴⁸ If dissociating hydroxyl groups were responsible for the pH dependence of the cation adsorption and retention properties of allophane then, like the clay minerals kaolinite, halloysite and gibbsite, it would also behave in some respects like a hydrous oxide.

Variations in the CEC between samples has depended upon their

composition, particularly the Si/Al ratio. This is a consequence of the difference in the ease of the ionisation of the hydroxyl groups; as silanol is weakly acidic, and aluminium hydroxide amphoteric, allophanes with larger Si/Al ratios have larger CEC's below saturation pH.⁴⁰ Some of this increase may be involved in the greater contribution that tetrahedral aluminium makes in the core of the siliceous allophane, i.e., the greater matrix negative charge. Some typical CEC values are given in Table 6.2.

Cation preferences on allophane have not been widely studied but the lyotropic series is usually followed at near neutral pH. Some observed preferences are: $\text{Ba}^{2+} > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+} > \text{NH}_4^+$;¹⁶⁴ $\text{Ca}^{2+} > \text{NH}_4^+$;²⁴² $\text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ ²⁴¹ and $\text{Rb}^+ > \text{K}^+$.²⁴¹ The interaction of allophane with potassium²⁴⁹ is similar to that observed for a synthetic aluminosilicate.²⁴⁵ This cation may be fixed and this has been thought to be linked to the magnesium deficiency in some allophane soils; the magnesium having been replaced by the potassium and leached out of the soil.²⁵⁰ Fixed potassium is beneficial in a soil as it is still usually available to plants but it is not lost by leaching. The loss of magnesium is not desirable however.

Most of the increase of the CEC with salt concentration may be due to increased exchange of cations for the protons of surface hydroxyl groups. A part of this increase has been found to be associated with aluminium displacement.²⁵¹

An important phenomenon reported by Wada and Harada²⁵² is the increase in CEC with temperature. The change observed between ambient and 50 - 60°C for allophane and imogolite was relatively large, that for kaolinite was moderate whilst only a very small change was noted for montmorillonite. These relative changes are also similar to the pH dependent variations and also suggest that the cation adsorption properties of these clays have different origins. The total

Table 6.2 Cation Exchange Capacities of some Soils and Clays

Material	Cation and conc. (M)	pH	CEC meq/100g	Ref.
<u>Soils</u>				
Allophane				
Dummore	Mg, 0.025	5.2	6.9	251
"	Ca, "	4.9	8.3	"
Oruanui	Mg, "	5.2	5.6	"
"	Ca, "	4.8	6.2	"
"	Ca, 0.05	4.8	7.3	"
Montmorillonite				
Arapohue	Ca, "	6.2	36.2	"
Allophane				
$\text{SiO}_2/\text{Al}_2\text{O}_3 = 2$	Ca, "	6.0	22.5	242
"	Ca, "	7.0	34.9	"
$\text{SiO}_2/\text{Al}_2\text{O}_3 = 1$	Ba, "	7.0	18.9	"
"	Ca, "	"	16.1	"
"	Mg, "	"	13.0	"
"	K, "	"	9.8	"
<u>Clays</u>				
Halloysite	NH_4^+ , 1.00	4 - 7	37	137
Montmorillonite-				
illite	NH_4^+ , "	"	46 - 50	"
Allophane	" "	4	20	"
"	" 0.20	5	6	"
"	" 0.50	"	10	"
"	" 1.50	"	30	"
"	" 0.20	7	23	"
"	" 0.50	"	30	"
"	" 1.00	"	40	"
"	" 1.50	"	52	"

effect was found to be only partially reversible so that material after wet heat treatment had a permanently enhanced CEC (and consequently an enhanced cation adsorption ability). The irreversibility may be associated with surface polymerisation of aluminous groups or association of anionic and cationic surface sites.^{242,252} Furthermore in an investigation of the rôle of the proton in the determination of CEC and AEC of allophane Harada and Wada²⁴² found that an increase in the CEC was always matched by a greater amount of hydrogen ion release but not by an increase in the AEC except when the increase arose from concentration changes.

Cation adsorption by allophane and by hydrous oxides is similar in some respects; the adsorption site appears to be associated with surface hydroxyl groups and H^+ is released upon adsorption.

6.4.5 Anion Adsorption

As most clay minerals have strong negative charges on their faces they do not readily bind anions to these parts; they may even be strongly repelled by them. Where positive surface charge can develop, for instance at edge sites, anion attraction can occur and so some clay minerals under differing conditions may exhibit both positive and negative anion adsorption.²⁵³⁻²⁵⁶ On montmorillonite positive adsorption of ions of low specificity such as chloride does not proceed significantly unless the pH is less than 6¹¹⁵ although on kaolinite the upper limit varies between pH 8 and 10.^{131,135,211} The adsorption of kaolinite and similar minerals, including allophane, is like that on the hydrous oxides and the amount bound increases approximately exponentially with decreasing pH.^{30,131,135,211} This is seen not only from the adsorption from dilute solution but also from Langmuir-type adsorption experiments at constant pH.^{158,204}

The treatment given a clay may have a strong influence upon its

ability to adsorb anions. When previously subjected to large quantities of phosphate or to processes which removed surface positive components such as iron(III) and octahedral aluminium a number of clays, including Tirau allophane, had their ability to bind anions drastically reduced and in some cases completely blocked.^{138,257} At the same time the cation adsorption capacity was greatly enhanced. The importance of the positive charge components to anion adsorption was also shown by the AEC enhancement observed when iron(III) hydroxide was added to kaolinite.¹³¹

Adsorption preferences have not been widely studied but they tend to parallel those for the hydrous oxides, i.e., high charge and ready hydrolysis induce strong adsorption. A significant difference from cation adsorption is that large diffuse anions are displaced by small anions, at least on montmorillonite where the following sequence was observed;²⁵⁸ $F^- > OH^- > H_2PO_4^- > Cl^- > CH_3CO_2^- \sim Br^- > NO_3^- > I^- > CNS^-$. The mechanism for adsorption of chloride and sulphate, and presumably also for the last five of the above series, is by surface protonation,¹⁵⁸ i.e., the first mechanism discussed for anion adsorption by hydrous oxides. The mode of interaction of the other three ions, and also selenite and arsenate, is by ligand exchange with the groups attached to matrix metal cations. The following sequence was found for a basaltic N.Z. clay;²⁵⁹ $HVO_3 > H_3PO_4 > H_2MoO_4 > H_2SO_4 > HCl$ (c.f. hydrous oxides, section 6.3.5).

Allophanic soils and clays can adsorb much larger quantities of anions than can those of the layer silicate minerals under comparable conditions. This is a result of the greater surface positive charge of allophane, a property derived from its surface hydrous oxides. The amount of anion adsorbed is dependent upon both concentration and pH; the adsorption of chloride and sulphate by a tropical allophanic soil increased with concentration up to a limiting value which itself

increased approximately exponentially with decreasing pH.¹⁵⁸ At pH near 5, and relatively high concentrations of free anion ($5 \times 10^{-2} \text{M}$), the amounts of chloride, sulphate and phosphate bound were about 5, 20 and 45 mmole/100g respectively. Chloride and sulphate appeared to adsorb in a manner mostly in response to surface protonation.

The adsorption of polyvalent anions such as phosphate and molybdate has aroused much interest because of their importance to soil fertility. The quantity of phosphate adsorbed by an allophanic soil has been found to be influenced by the extent of its hydrolysis, i.e., the effect of pH is not only on the surface charge but also on the anion itself.¹⁵⁸ Adsorption of selenite, phosphate and molybdate from dilute solutions onto allophane clay could be described by a single term Langmuir equation.¹⁶¹ Under these conditions the adsorption proceeded by exchange for adsorbed sulphate, silicate, aquo and hydroxyl groups.^{159,168} At high concentrations however phosphate alone continued to be adsorbed by displacement of structural silicate and possibly also by disruption of hydrous oxide polymers. This adsorption was able to be described by a two-term Langmuir equation which differentiated between the two sorption mechanisms. The intensity of the interaction was such that phosphate may become fixed and almost completely unavailable to the soil solution.

The large anion adsorption capacity of allophane, and similar poorly ordered and amorphous materials, has been used to estimate its presence in soils by an exchange technique. When neutral sodium fluoride solution interacts with allophane the fluoride replaces surface hydroxyl groups which are released and the pH increases. The "allophane test" utilises this reaction in the presence of the pH indicator phenolphthalein; the rapid appearance of a strong pink colouration is taken as being a positive identification of allophane.²⁶⁰ More precise methods for lower concentrations of the material depend

upon measuring the amount of hydroxide freed. Perrott *et al.*²⁶¹ showed that the amount of acid consumed in maintaining the pH constant for 25 minutes after addition of a soil sample to a 0.85M solution of sodium fluoride had a high correlation with the content of non-crystalline and poorly ordered components of a large number of soils.

6.4.6 A Summary of pH Dependent Cation Adsorption by Clays

A simple description of the pH dependence of cation adsorption at the clay/aqueous interface can be drawn up as follows:

At low pH cations appear to be interacting with the more acid components and the permanent negative charges of the clay. Cations retained by these sites are generally reversibly bound as hydrated entities with a binding strength related to the cation charge and size.

Increasing the pH increases the surface negative charge by deprotonation of surface hydroxyl groups; this promotes further electrostatic attraction and complex formation between the surface and the cation although complex formation does not usually proceed unless the pH is sufficiently high as to allow cation hydrolysis to occur. Hydrolysis in turn not only reduces the ion solvation energy, which promotes adsorption by materials with low dielectric constant, but also increases surface complex formation.

At higher pH precipitation of the cation as its hydroxide may occur. The surface then takes on characteristics of the precipitated hydroxide.

6.5 Conclusion

Although the interactions of allophane with cations appear to show many similarities to the hydrous oxide-cation interactions a number of

phenomena associated with this process are not understood. For instance, there is the influence of the surface aluminium hydroxide, the extent of cation adsorption from dilute solution at variable pH and the nature of the cation properties that affect cation selectivity. Furthermore, no mathematical basis is currently available to enable adsorption behaviour to be predicted.

CHAPTER SEVEN

AN IMPROVED MODEL FOR ION ADSORPTION BY HYDROUS OXIDES

7.1 Introduction

Mathematical models that describe chemical systems have been sought because they allow a greater understanding of the nature and mechanisms of the systems. They also permit both the results of changes within a system and the behaviour beyond the regions of direct measurement to be predicted.

Such models may be empirical, e.g., the Freundlich adsorption isotherm or Bilinski's equation for the adsorption of hydrolysing species by hydrous oxides.²⁶² Alternatively they may be derived from mechanistic considerations, e.g., the Langmuir and BET adsorption models.

No model is currently available to describe the adsorption of cations from solution by allophane. As clays containing this mineral display similar ion adsorption properties to the hydrous oxides, models that describe the interactions of ions with hydrous oxides were investigated. The presently accepted models have a number of shortcomings that make them unsuitable for general application. Some of these models are discussed briefly in the next section.

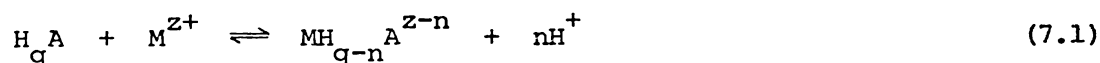
A Stern-type model that has successfully described the variation of surface charge at the silica surface is investigated in section 7.2.3 and the anticipated behaviour of the adsorbing electrolyte is now clear. To allow application to allophane this model needed to be further extended to include multivalent cations, mixtures of cations and the influence of the presence of a hydroxide like aluminium hydroxide.

7.2 Ion Adsorption Models:- The Present State

7.2.1 The Mass Action Model

It has been found that the mass action approach to cation adsorption at the clay mineral surface has provided a reasonable description of the exchange of some cations at relatively strong acid ion exchange sites, already saturated with some other cation.^{147,168,226}

Kurbatov et al.²⁶³ in 1951 applied this approach to the adsorption of a number of divalent cations on hydrous iron(III) oxide. The more generalised equilibrium proposed between the cation M^Z and the hydrous oxide surface group H_qA can be represented by;



n is the number of hydrogen ions apparently released per cation adsorbed. If the total concentration of possible sites for adsorption is N_o then by application of the mass action concept the equilibrium constant, K , for (7.1) is given by;

$$K = \frac{(N_o - [H_qA])}{[H_qA]} \cdot \frac{[H^+]^n}{[M^{Z+}]} \quad (7.2)$$

The partitioning of the cation between the two phases is described by the distribution coefficient, D , which is the relative amount of the cation in each state;

$$D = \frac{(N_o - [H_qA])}{[M^{Z+}]} \quad (7.3)$$

$$\therefore \log D = \log K + \log [H_qA] + n \text{ pH} \quad (7.4)$$

For systems where only a small number of adsorption sites are occupied, i.e., $[H_qA] \rightarrow N_o$, the plot of $\log D$ against pH would be linear with a slope, n , that would equal the apparent number of hydrogen ions released by each adsorbing cation.

Using this basis n has been found, for the adsorption of some divalent cations onto some hydrous metal oxides, to be; 1 for dilute solution in dilute electrolyte but decreasing to 0.7 when the cation concentration was raised to 10^{-3} M, or the electrolyte to 1 M;²⁶⁴ 1.0 at low cation concentration, but decreasing to 0.2 for 5×10^{-2} M solution;²⁶⁵ and various values between 0.8 and 1.7 depending upon the cation, the adsorbent and the pH range.¹⁸⁰

Kolarik²⁶⁵ proposed that the variation of this number with the concentration of the cation was the result of the formation of "multinuclear" adsorption complexes where one adsorption site bound more than one cation but released only one H^+ . However it can be shown that if this assumption is made the derivation $d \log D/d \text{ pH}$ is no longer constant over the whole pH range and changes value at the pH where $\log D = 0$ (Appendix III). This change has not been observed experimentally and so this theory does not hold.

Although plots of $\log D$ against pH suggest that the exchange of a divalent cation is for about one H^+ , direct measurements have shown that the actual amount released is greater; generally near two.¹⁸⁹ Furthermore aluminium adsorption on clay minerals has been accompanied by the release of 3 moles of acid per mole adsorbed,²⁶⁶ whilst on a manganese oxide adsorption of a divalent cation was a quantitative exchange for H^+ , Na^+ , and K^+ .¹⁹⁹ It would appear that cation adsorption by hydrous oxides is frequently a stoichiometric ion exchange; for surfaces with low concentrations of other adsorbed cations the exchange is for H^+ . In (7.1) it follows that generally $n = z$.

7.2.2 Electrochemical Models

A major criticism of the simple mass action approach is that it considers the chemical potential of all species to be related only to

their concentration (or activity); the electrical influences present are ignored. At strong acid adsorption sites, such as those of most common ion exchange resins, this is reasonable as all ions may occupy the same position and so experience the same electrical potentials. At a charged surface this is not necessarily true, especially if the exchange is between ions from different parts of the double layer. (The electrical double layer is described in Chapter Four.)

The partitioning of a non-potential determining ion between a solution and a charged interface has been discussed by Stern⁹⁴ (see section 4.5.3 and equation (4.22)). His theory was subsequently improved by Grahame,⁹⁵ but neither worker (nor more recently James and Healy¹⁰⁴ and Bowden et al.¹¹⁰) has considered the adsorption process to be an exchange. That this was the case for hydrous oxides has been recognised by Forbes et al.¹⁸⁹ and Yates et al.²⁶⁷ in their models. Although both treatments are similar (they are both "Stern-type"), the site-binding model of Yates et al. is the more thorough; it does not presuppose the validity of the Nernst equation (see section 4.6). In their treatment Yates et al. were concerned only with the adsorption of the potential determining ions, H^+ and OH^- , at the hydrous oxide surface in the presence of an indifferent electrolyte. The adsorption behaviour of the electrolyte was not revealed.

7.2.3 The Site-Binding Model of James, Levine and Healy²⁶⁹

The adsorption of simple monovalent ions at the hydrous oxide/aqueous interface occurs at a surface charged by the adsorption of either H^+ or OH^- . As adsorption of OH^- is perhaps better represented by desorption of H^+ the surface charging reactions are;



where HA , H_2A^+ and A^- are discrete neutral, positive and negative surface groups, respectively. These surface charges are balanced by the adsorption of monovalent cations M^+ or anions X^- , from the electrolyte MX , into the inner Helmholtz plane (IHP) (see section 4.5.3, fig. 4.2) to form interfacial ion-pairs. The processes by which this can proceed are;



where AM and H_2AX are interfacial ion pairs with the adsorbed ion lying in the IHP. Thus the cation M^+ when adsorbed is a distance β_m from the surface and the anion X^- a distance β_x . For this system the electrochemical potential of each ion can be obtained from (4.4) (but with $\psi_0 = \psi + \chi$), for the charged surface sites A^- and H_2A^+ , and for the adsorbed cation and anion with $\psi + \chi$ replaced by $\psi_{\beta m}$ or $\psi_{\beta x}$, the potentials experienced by each in the IHP, respectively. Equilibrium for the above four processes, as the difference between the electrochemical potentials of species i in the two states is zero, therefore;

$$\mu_{i(soln)} = \mu_{i(surf)} \quad (7.9)$$

Thus the following relationships hold (concentrations have used in lieu of activities);

$$kT \ln \frac{[HA]}{[A^-]} + \mu_{HA}^0 = \mu_A^0 + \mu_H^0 + kT \ln [H^+] - e\psi_0 \quad (7.10)$$

$$kT \ln \frac{[HA]}{[H_2A^+]} + \mu_{HA}^0 + \mu_H^0 = \mu_{H_2A}^0 - kT \ln [H^+] + e\psi_0 \quad (7.11)$$

$$\begin{aligned} kT \ln \frac{[H_2A^+]}{[H_2AX]} + \mu_{H_2A}^0 + \mu_X^0 + kT \ln [X^-] + e\psi_0 \\ = \mu_{H_2AX}^0 + e\psi_0 - e\psi_{\beta x} \end{aligned} \quad (7.12)$$

$$\begin{aligned}
 kT \ln \frac{[A^-]}{[AM]} + \mu_A^0 + \mu_M^0 + kT \ln [M^+] - e\psi_0 \\
 = \mu_{AM}^0 - e\psi_0 + e\psi_{\beta m}
 \end{aligned}
 \quad (7.13)$$

where μ_i^0 is the standard chemical potential of species i . The equilibrium constant for an equilibrium reaction can be obtained from the relationship $\mu_i^0 = -kT \ln K$. If K_- and K_+ are the equilibrium constants for the processes (7.5) and (7.6), and K_x and K_m are the dissociation constants for the ion pairs H_2AX and AM respectively then;

$$K_+ = \exp.(\mu_{H_2A}^0 - \mu_{HA}^0 - \mu_H^0)/kT \quad (7.14)$$

$$K_- = \exp.(\mu_{HA}^0 - \mu_A^0 - \mu_H^0)/kT \quad (7.15)$$

$$K_x = \exp.(\mu_{H_2AX}^0 - \mu_{H_2A}^0 - \mu_X^0)/kT \quad (7.16)$$

$$K_m = \exp.(\mu_{AM}^0 - \mu_A^0 - \mu_M^0)/kT \quad (7.17)$$

(7.10) to (7.12) can now be rearranged;

$$[HA] = [H_2A^+] \Omega_+ \quad ; \quad \Omega_+ = \frac{K_+}{[H^+]} \exp\left(\frac{e}{kT} \psi_0\right) \quad (7.18)$$

$$[HA] = [A^-] \Omega_- \quad ; \quad \Omega_- = \frac{[H^+]}{K_-} \exp\left(-\frac{e}{kT} \psi_0\right) \quad (7.19)$$

$$[H_2AX] = [H_2A^+] \Omega_x \quad ; \quad \Omega_x = \frac{[X^-]}{K_x} \exp\left(\frac{e}{kT} \psi_{\beta x}\right) \quad (7.20)$$

$$[AM] = [A^-] \Omega_m \quad ; \quad \Omega_m = \frac{[M^+]}{K_m} \exp\left(-\frac{e}{kT} \psi_{\beta m}\right) \quad (7.21)$$

The functions Ω_i , functions of the solution concentrations of the adsorbing species, the equilibrium constant for the formation of the adsorption complex and the electrical potential term, have been

introduced for convenience. The various equilibrium constants for the formation of the adsorption complexes, K_i , incorporated not only the term for coulombic interaction between both parts of the interfacial ion pair but also the specific adsorption potentials, $\phi^\pm$, of (4.22) or (4.28); i.e., $\Omega_m = [M^+] E^+$ and $\Omega_x = [X^-] E^-$.

If the total concentration of surface hydroxyl groups is N_o then;

$$N_o = [H_2AX] + [H_2A^+] + [HA] + [A^-] + [AM] \quad (7.22)$$

and the surface charge, σ_o , is given by;

$$\sigma_o = f \cdot ([H_2AX] + [H_2A^+] - [A^-] - [AM]) / A_v \quad (7.23)$$

where A_v is the specific area per unit volume of suspension. (This is needed as, for simplicity, all other concentrations have been defined as moles per unit volume.) If it is assumed that both the anion and the cation adsorb in the same plane, i.e., $\beta_m = \beta_x$, the charge in the IHP is;

$$\sigma_\beta = f \cdot ([AM] - [H_2AX]) / A_v \quad (7.24)$$

Using (7.18) to (7.21) and (4.24) to (4.27) it is possible to get a complete solution to the double layer equations. This was done by Yates *et al.*²⁶⁷ and the calculated plots of both σ_o and ψ_d against pH were very similar to experiment. No indication of the adsorption behaviour of the electrolyte was given except that it was required to lie close to the surface, perhaps almost on the same plane as the adsorbed p.d. ions, as suggested by de Bruyn and co-workers.^{106, 144}

7.3 An Attempt to Extend the Site-Binding Model

In this section the adsorption of the indifferent electrolyte predicted by the site-binding model of the electrical double layer at

the hydrous oxide/aqueous interface, as described in the previous section, is revealed. The treatment is then extended to multivalent cations, mixtures of cations and cation adsorption in the presence of a slightly soluble hydroxide.

7.3.1 The Adsorption of Monovalent Electrolytes

The total concentration of surface groups, N_o , is the sum of their concentrations in the five available surface states. Using the exponential functions defined by (7.18) to (7.21) and incorporating them into (7.22) yields;

$$N_o = [AM] \left(1 + \frac{1}{\Omega_m} (1 + \Omega_- (1 + \frac{1}{\Omega_+} (1 + \Omega_x))) \right) \quad (7.25)$$

$$= [AM] \left[1 + \frac{1}{\Omega_m} + \frac{\Omega_-}{\Omega_m} + \frac{\Omega_-}{\Omega_m \Omega_+} + \frac{\Omega_- \Omega_x}{\Omega_m \Omega_+} \right] \quad (7.26)$$

The relationship (7.26) expresses the distribution of the surface sites in each of the five states; AM, A^- , HA, H_2A^+ , H_2AX . (The similarity of (7.26) to the Stern equation is shown in Appendix III.)

A convenient representation of experimental results has been the plot of the logarithm of the distribution coefficient, $\log D$ (where $D = [AM]/[M^+]$), against pH. These plots have often been linear,^{180,191,263-265} and so the derivative $d \log D/d \text{ pH}$ has been constant. A requirement of any model is that it should also satisfy this condition for typical situations.

In (7.26) as Ω_x and Ω_m are functions not only of $[X^-]$ and $[M^+]$ but also of pH (via $\psi_{\beta x}$ and $\psi_{\beta m}$) then with pH change the adsorption behaviour of the cation and the anion will go through different stages. There are five possibilities of consequence depending upon which state dominates the surface. This in turn will depend upon the values of the exponential functions, Ω_i , themselves functions of the pH and the

concentration of the electrolyte components.

Condition (i): high pH and high electrolyte concentrations; from (7.18) to (7.21);

$$1 \gg \frac{1}{\Omega_m} + \frac{\Omega_-}{\Omega_m} + \dots \quad (7.27)$$

$$\text{i.e. } \Omega_m \gg 1, \Omega_m \gg \Omega_-, \Omega_+, \Omega_x \ll 1$$

$$\therefore [AM] = N_o \quad (7.28)$$

$$\text{and } \log D = \log (N_o/[M^+]).$$

Differentiating with respect to pH produces;

$$\frac{d \log D}{d \text{ pH}} = 0 \quad (7.29)$$

Under these conditions all surface sites are deprotonated and occupied by cations (i.e., as AM) in which case the slope of the log D/pH plot is zero. D is now a function of $[M^+]$.

Condition (ii): high pH and low electrolyte concentration or low adsorption potential; from (7.18) to (7.21);

$$\frac{1}{\Omega_m} \gg 1 + \frac{\Omega_-}{\Omega_m} + \dots \quad (7.30)$$

$$\text{i.e. } \Omega_m \ll 1, \Omega_m \ll \Omega_-, \Omega_+ \gg \Omega_-, \Omega_x \ll 1$$

$$\therefore [AM] = N_o \Omega_m = \frac{N_o [M^+]}{K_m} \exp\left(-\frac{e}{kT} \psi_{\beta m}\right) \quad (7.31)$$

$$\log D = \log N_o - \log K_m - \frac{e}{kT} \psi_{\beta m} \quad (7.32)$$

$$\therefore \frac{d \log D}{d \text{ pH}} = -\frac{e}{2.3kT} \frac{d\psi_{\beta m}}{d \text{ pH}} \quad (7.33)$$

This situation could only occur at sufficiently high pH for the adsorbed cations to occupy only a small part of the surface or if the

cation is unwilling to form an ion pair with the surface. The surface would be highly dissociated (i.e., mostly A^-) and the amount of a cation adsorbed would be dependent upon its concentration. D is now independent of $[M^+]$.

Condition (iii): moderate pH and low electrolyte concentrations; from (7.18) to (7.21);

$$\frac{\Omega_-}{\Omega_m} \gg 1 + \frac{1}{\Omega_m} + \dots \quad (7.34)$$

$$\text{i.e. } \Omega_- \gg \Omega_m, \Omega_- \gg 1, \Omega_+ \gg 1, \Omega_x \ll 1$$

$$\therefore [AM] = N_o \frac{\Omega_m}{\Omega_-} = N_o \frac{[M^+] K_-}{[H^+] K_m} \exp\left(\frac{e}{kT} (\psi_o - \psi_{\beta m})\right) \quad (7.35)$$

$$\log D = \log N_o + \log \frac{K_-}{K_m} + \text{pH} + \frac{e}{2.3kT} (\psi_o - \psi_{\beta m}) \quad (7.36)$$

$$\therefore \frac{d \log D}{d \text{pH}} = 1 + \frac{e}{2.3kT} \frac{d}{d \text{pH}} (\psi_o - \psi_{\beta m}) \quad (7.37)$$

At moderate pH the surface is mostly neutral, HA , or about equivalently ionised as H_2A^+ and A^- . Each cation adsorbing will exchange for one proton and each adsorbing anion will be accompanied by the adsorption of another proton. Furthermore the quantity of cation adsorbed will be dependent upon its concentration, i.e., D is independent of $[M^+]$ except insofar as $[M^+]$ influences ψ_o or $\psi_{\beta m}$.

Condition (iv): low pH and low electrolyte concentration or low anion adsorption potential; from (7.18) to (7.21);

$$\frac{\Omega_-}{\Omega_m \Omega_+} \gg 1 + \frac{1}{\Omega_m} + \dots \quad (7.38)$$

$$\text{i.e. } \Omega_+ \ll 1, \Omega_x \ll 1, \Omega_- \gg \Omega_m \Omega_+$$

$$\therefore [AM] = N_o \frac{\Omega_m \Omega_+}{\Omega_-} = N_o \frac{[M^+]_{-K_+}}{[H^+]^2_{K_m}} \exp\left(\frac{e}{kT} (2\psi_o - \psi_{\beta m})\right) \quad (7.39)$$

$$\log D = \log N_o + \log \frac{K_- K_+}{K_m} + 2 \text{ pH} + \frac{e}{2.3kT} (2\psi_o - \psi_{\beta m}) \quad (7.40)$$

$$\therefore \frac{d \log D}{d \text{ pH}} = 2 + \frac{e}{2.3kT} \frac{d}{d \text{ pH}} (2\psi_o - \psi_{\beta m}) \quad (7.41)$$

At low pH the surface is mostly protonated and so adsorption of a cation would be accompanied by release of two protons. Again the tendency for cations to adsorb is low and the quantity adsorbed is dependent upon the concentration, i.e., D is independent of $[M^+]$. This situation is analogous to condition (ii) except that the charges are reversed.

Condition (v): very low pH and high electrolyte concentration;
from (7.18) to (7.21);

$$\frac{\Omega_- \Omega_x}{\Omega_+ \Omega_m} \gg 1 + \frac{1}{\Omega_m} + \dots \quad (7.42)$$

i.e. $\Omega_x \gg 1$, $\Omega_+ \ll 1$, $\Omega_- \gg 1$, $\Omega_m \ll 1$.

$$\therefore [AM] = N_o \frac{\Omega_m \Omega_+}{\Omega_x \Omega_-} = N_o \frac{[M^+]_{K_- K_+ K_x}}{[H^+]^2_{K_m}} \exp\left(\frac{e}{kT} (2\psi_o - \psi_{\beta m} - \psi_{\beta x})\right) \quad (7.43)$$

$$\begin{aligned} \log D = \log N_o + \log \frac{K_- K_+ K_x}{K_m} + 2 \text{ pH} + \log[X^+] \\ + \frac{e}{2.3kT} (2\psi_o - \psi_{\beta m} - \psi_{\beta x}) \end{aligned} \quad (7.44)$$

$$\therefore \frac{d \log D}{d \text{ pH}} = 2 + \frac{e}{2.3kT} \frac{d}{d \text{ pH}} (2\psi_o - \psi_{\beta m} - \psi_{\beta x}) + \frac{d \log[X^-]}{d \text{ pH}} \quad (7.45)$$

At very low pH the surface would become saturated with adsorbed anions and so adsorption of a cation would require the exchange of two

protons and an anion.

Both of the last two situations are of little significance except perhaps at low pH; they will not be considered in depth again.

In all cases, except when the surface is completely saturated with cation, the derivative, $d \log D/d \text{ pH}$, is positive and so the amount of cation adsorbed will increase with pH. Furthermore the influence of a change in pH has a greater relative effect at lower pH than at high. From (7.22) and (7.23) as the pH increases the surface charge becomes progressively more negative and the charge in the IHP more positive.

In the absence of strong acid or high surface concentrations of the anion there are three regions displaying differing cation adsorption behaviour. Such a system may have been observed by Allen and Matijević¹⁹¹ for the adsorption of sodium onto silica over a wide pH range (see fig. 7.1). At low pH near the PZC $\log D$ was observed to be linear with pH; the slope was 1.0. This result was interpreted, using the mass action approach,²⁶⁸ as indicating that the exchange was for a single H^+ . In terms of the site binding model, however, it would also be noted that upon adsorption the sodium ion occupied a position electrically equivalent to that vacated by H^+ , i.e., $\psi_{\beta m} = \psi_0$; in the low pH region the adsorption might be described adequately by (7.35).

In neutral and alkaline systems $\log D$ was still linear with pH, but with a reduced gradient. Furthermore it was no longer independent of the cation concentration. In fact $\log D$ decreased with increasing cation concentration as if the surface was saturated although greater adsorption was found at higher pH. From this observation it is apparent that only a definite amount of the surface can be occupied at any pH; the amount increasing approximately exponentially with pH up to complete surface saturation in a manner similar to that found

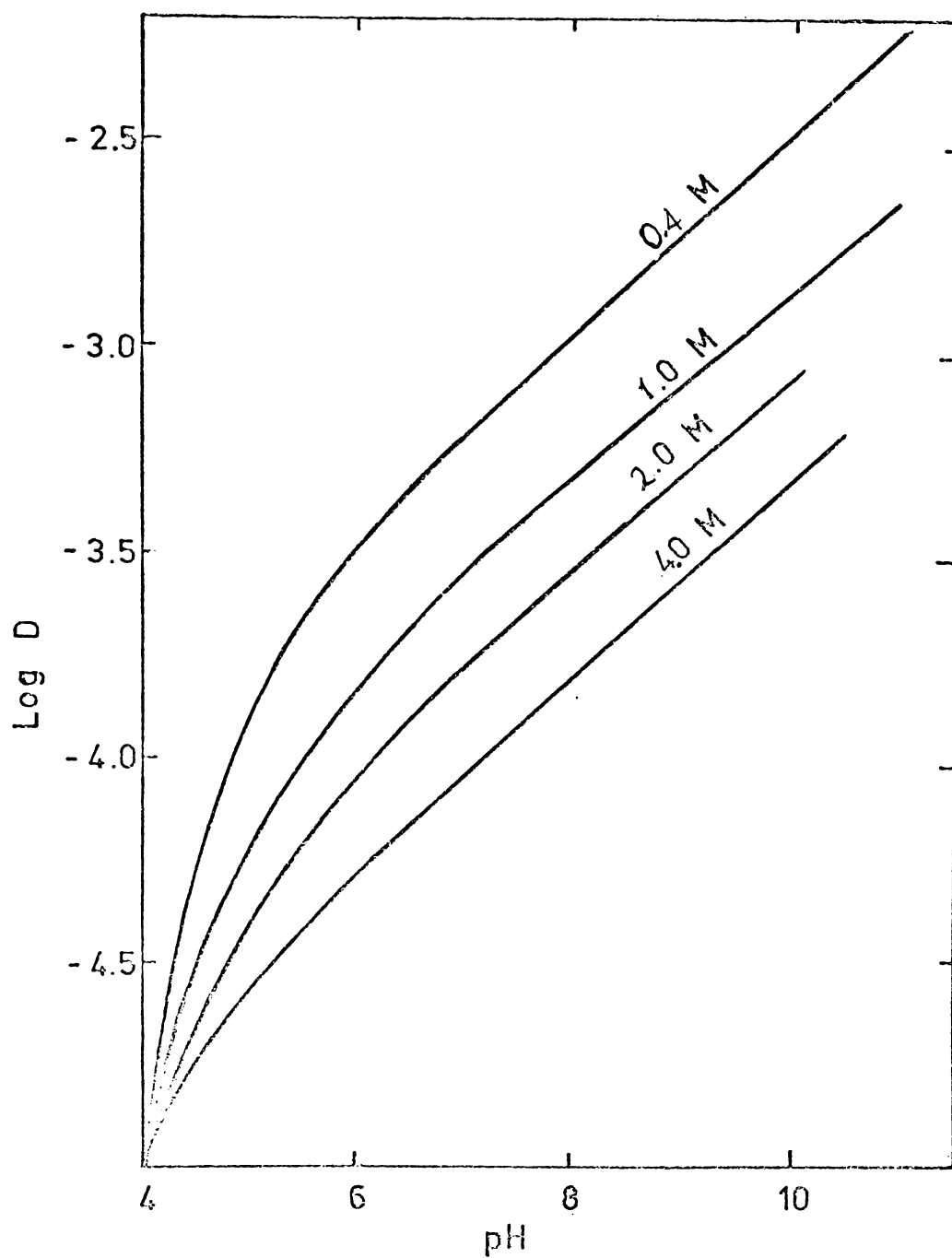


Figure 7.1. Adsorption of sodium by Ludox HS silica at four different concentrations of NaCl. (Redrawn from ref. 191.)

with other hydrous oxides (see section 6.3.4). The explanation offered for this behaviour was that it was due to a combination of the existence of two adsorption site types of different binding energy and equilibrium constants for the adsorption reaction that varied with surface occupancy and resisted adsorption as saturation was approached.²⁶⁸ These suggestions are reasonable but they do require the application of non-linear functions to describe what appears to be a linear relationship.

That the second region of linear dependence of $\log D$ upon pH in figure 7.1 is not associated with condition (ii) here is implied by the pH at which the two linear parts meet. From (7.30) and (7.34), this would be at the pH where $\Omega_- = 1$. As hydrous oxides, such as silica, are constant potential materials the Nernst equation (4.6) may hold approximately and so, from (7.19), Ω_- and pH will be constant. That is, the pH where the two linear parts of figure 7.1 meet would also be constant; it should not vary with cation concentration as observed.

The existence of a region described by (7.30) and (7.33) is also unlikely as it requires a solution of high alkalinity to induce a high degree of dissociation of surface groups. This in turn requires a high cation concentration and provides the opportunity for adsorption to proceed at the IHP. If large charge densities could occur in the diffuse layer this would stabilise a highly dissociated surface but large diffuse layer charges are not consistent with electrokinetic studies.²⁶⁷ The highly dissociated surface may not be significant with hydrous oxides.

In a much simplified electrochemical theory of the hydrous oxide/aqueous interface Bowden *et al.*¹¹⁰ observed that the predicted maximum adsorption increased exponentially with pH. This is in agreement with the experimental observations for such systems (see

also section 6.3.4). A full solution of the site-binding model is expected to show the same results.

7.3.2 The Adsorption of Multivalent Cations; Fixed Surface Groups

The adsorption of multivalent cations is complicated by a difficulty experienced in defining the adsorption sites. For simplicity the two extreme situations for the equivalent exchange of H^+ for the adsorbing cation M^{z+} will be considered. In this section the exchange will be considered to be from z fixed neighbouring hydroxyl groups, i.e., $(HA)_z$ or $(H_z A_z)$. In the next section they will be considered to be quite free and independent. In both cases it is assumed that the adsorption of a z -valent cation can occur only after the loss of z H^+ ions from neutral groups. (This is not necessarily always true.¹⁹²)

Provided there are no significant charge transfer processes operating through the solid it will be assumed that the individual hydroxyl groups can ionise independently; an ionisation reaction at one group interacts upon its neighbours only through the surface potential. The adsorption site will act as a z -dentate ligand with the z groups ionising independently from their fixed positions. Adsorption of M^{z+} can only proceed at a site if all the groups are deprotonated, i.e., the site is in the form A_z^{z-} . If the anion is still a monovalent indifferent species X^- the possible reactions that may occur are, for surface ionisation;



...





...



and for ion adsorption;



...



Adsorption in the region of low pH where anion influences upon cation adsorption may be significant will not be considered.

The equilibrium conditions for the dissociation reactions (7.46) to (7.51) are;

$$kT \ln \frac{[H_z A_z]}{[H_{z-1} A_z^-]} + \mu_{A_z H_z}^0 = \mu_{H_{z-1} A_z}^0 + \mu_H^0 + kT \ln[H^+] - e\psi_0 \quad (7.57)$$

$$\begin{aligned} kT \ln \frac{[H_{z-1} A_z^-]}{[H_{z-2} A_z^{2-}]} + \mu_{H_{z-1} A_z}^0 - e\psi_0 \\ = \mu_{H_{z-2} A_z}^0 + \mu_H^0 + kT \ln[H^+] - 2e\psi_0 \end{aligned} \quad (7.58)$$

...

$$\begin{aligned}
 kT \ln \frac{[H_z A_z^{1-z}]}{[A_z^{z-}]} + \mu_{HA_z}^0 + (1-z)e\psi_0 \\
 = \mu_{A_z}^0 + \mu_H^0 + kT \ln[H^+] - ze\psi_0
 \end{aligned} \quad (7.59)$$

For which the equilibrium constants are;

$$K_{(7.46)} = \exp((\mu_{H_z A_z}^0 - \mu_{H_{z-1} A_z}^0 - \mu_H^0)/kT) \quad (7.60)$$

$$K_{(7.47)} = \exp((\mu_{H_{z-1} A_z}^0 - \mu_{H_{z-2} A_z}^0 - \mu_H^0)/kT) \quad (7.61)$$

...

$$K_{(7.51)} = \exp((\mu_{HA_z}^0 - \mu_{A_z}^0 - \mu_H^0)/kT) \quad (7.62)$$

As it has been assumed that each hydroxyl group can dissociate independently of its neighbours;

$$\begin{aligned}
 \mu_{H_z A_z}^0 - \mu_{H_{z-1} A_z}^0 &= \mu_{H_{z-1} A_z}^0 - \mu_{H_{z-2} A_z}^0 = \dots\dots\dots \\
 &= \mu_{HA_z}^0 - \mu_{A_z}^0 = \mu_{HA}^0 - \mu_A^0
 \end{aligned} \quad (7.63)$$

$$\text{i.e. } K_{(7.46)} = K_{(7.47)} = \dots\dots\dots = K_{(7.51)} = K_- \quad (7.64)$$

Thus it follows that;

$$[HA_z^{1-z}] = [A_z^{z-}] \Omega_-^z; \dots\dots; [H_z A_z] = [A_z^{z-}] \Omega_-^z \quad (7.65)$$

Similarly it can be shown that;

$$[H_{z+1} A_z^+] = [A_z^{z-}] \frac{\Omega_+^z}{\Omega_-^z}; \dots\dots; [H_{2z} A_z^{z+}] = [A_z^{z-}] \frac{\Omega_+^z}{\Omega_-^z} \quad (7.66)$$

$$[H_{z+1}A_zX] = [A_z^{z-}] \frac{\Omega_z^z \Omega_x}{\Omega_+^z}; \dots; [H_{2z}A_zX_z] = [A_z^{z-}] \frac{\Omega_z^z \Omega_x^z}{\Omega_+^z} \quad (7.67)$$

The equilibrium expression for the cation adsorption is now;

$$\begin{aligned} kT \ln \frac{[A_z^{z-}]}{[A_zM]} + kT \ln[M^+] + \mu_{A_z}^o + \mu_m^o - ze\psi_o \\ = \mu_{A_zM}^o + ze\psi_{\beta m} - ze\psi_o \end{aligned} \quad (7.68)$$

But the dissociation constant for A_zM , K_m , is given by;

$$K_m = \exp((\mu_{A_zM}^o - \mu_m^o - \mu_{A_z}^o)/kT) \quad (7.69)$$

$$\therefore [A_zM] = [A_z^{z-}] \Omega_m; \quad \Omega_m = \frac{[M^{z+}]}{K_m} \exp(-\frac{ze}{kT} \psi_{\beta m}) \quad (7.70)$$

If the total concentration of surface reactive hydroxyl groups is N_o then the total concentration of possible sites for cation adsorption is;

$$\begin{aligned} \frac{N_o}{Z} = & [A_zM] + [A_z^{z-}] + [HA_z^{z-1}] + \dots + [H_{z-1}A_z^-] + [H_zA_z] \\ & + [H_{z+1}A_z^+] + [H_{z+2}A_z^+] + \dots + [H_{2z}A_z^{z+}] \\ & + [H_{z+1}A_zX] + [H_{z+2}A_zX^+] + \dots + [H_{2z}A_zX^{z-1}] \\ & + [H_{z+2}A_zX_2] + \dots + [H_{2z}A_zX_2^{z-2}] + \dots + [H_{2z}A_zX_z] \end{aligned} \quad (7.71)$$

$$\begin{aligned} = & [A_zM] + \sum_{i=0}^{z-1} [H_iA_z^{i-z}] + [H_zA_z] + \sum_{i=1}^z [H_{z+i}A_z^{i+}] \\ & + \sum_{i=1}^z \sum_{j=1}^i [H_{z+i}A_zX_j^{i+j}] \end{aligned} \quad (7.72)$$

By using the expressions that can be generated for each possible site state as in (7.65) to (7.67) and utilising (7.70) and (7.72) the total number of possible sites for cation adsorption can be obtained as a function of the function of the concentration of adsorbed cation, $[A_z M]$;

$$\begin{aligned} \frac{N_o}{z} = [A_z M] & \left(1 + \frac{1}{\Omega_m} + \frac{\Omega_-}{\Omega_m} (1 + \Omega_- (1 + \dots \dots \right. \\ & \left. + \Omega_- (1 + \frac{1}{\Omega_+} (1 + \frac{1}{\Omega_+} (1 + \dots \dots))) \dots \dots) \right) \end{aligned} \quad (7.73)$$

$$= [A_z M] \left(1 + \frac{1}{\Omega_m} \cdot \frac{\Omega_-^z - 1}{\Omega_- - 1} + \frac{\Omega_-^z}{\Omega_m} \cdot \frac{\Omega_+^{-z} - 1}{\Omega_+^{-1} - 1} \right) \quad (7.74)$$

It can be seen that as each term in (7.74) except the first involves exponential functions of $[H^+]$ the complete equation can be simplified under a number of conditions, notably pH and cation concentrations. Four terms are present; it will be remembered that five terms occurred in the monovalent case but adsorbing anion has been omitted here. Again the condition for saturation is of little interest and the next condition (highly dissociated) has no experimental confirmation of its existence. Similarly the low pH situation may be neglected. This leaves only the condition for adsorption at pH near PZC with low cation concentrations, condition (iii) above;

$$\text{Here } \frac{\Omega_-^z}{\Omega_m} \gg 1 + \dots \dots \quad (7.75)$$

i.e. $\Omega_- \gg 1, \Omega_- \gg \Omega_m, \Omega_+ \gg 1.$

$$[A_z M] = \frac{N_o}{z} \frac{\Omega_m}{\Omega_-^z} = \frac{N_o [M^{z+}] K_-^z}{z [H^+]^z K_m} \exp\left(\frac{ze}{kT} (\psi_o - \psi_{\beta m})\right) \quad (7.76)$$

$$\log D = \log \frac{N_o}{z} + \log \frac{K_m^z}{K_m} + z\text{pH} + \frac{ze}{2.3kT} (\psi_o - \psi_{\beta m}) \quad (7.77)$$

$$\frac{d \log D}{d \text{pH}} = z + \frac{ze}{2.3kT} \frac{d}{d \text{pH}} (\psi_o - \psi_{\beta m}) \quad (7.78)$$

These equations are identical to (7.35) to (7.37) except for the inclusion of the ion charge z . This particular situation will be considered in more detail in section 7.3.4.

7.3.3 The Adsorption of Multivalent Cations; Independent Surface Groups

An alternate approach to multivalent cation adsorption is to consider the adsorption site to be made of z quite independent surface groups which ionise independently and influence each other only via the surface potential. The adsorption reaction for M^{z+} is now;



for which the equilibrium condition is;

$$\begin{aligned} kT \ln \frac{[A_z M]}{[A^-]^z} + \mu_{A_z M}^o + ze\psi_{\beta m} - ze\psi_o \\ = kT \ln [M^{z+}] + z\mu_A^o + \mu_m^o - ze\psi_o \end{aligned} \quad (7.80)$$

but the equilibrium constant is;

$$K_m = \exp((\mu_{A_z M}^o - \mu_m^o - z\mu_A^o)/kT) \quad (7.81)$$

$$\therefore [A_z M] = [A^-]^z \Omega_m; \quad \Omega_m = \frac{[M^{z+}]}{K_m} \exp(-\frac{ze}{kT} \psi_{\beta m}) \quad (7.82)$$

If the total concentration of exchangeable surface hydroxyl groups is N_o then;

$$N_o = z [A_z M] + [A^-] + [HA] + [H_2 A^+] + [H_2 AX] \quad (7.83)$$

Using (7.18) to (7.21) and (7.82) then;

$$N_o = z [A_z M] + \frac{[A_z M]^{\frac{1}{z}}}{(\Omega_m)^{\frac{1}{z}}} (1 + \Omega_- (1 + \frac{1}{\Omega_+} (1 + \Omega_x))) \quad (7.84)$$

If, for the same reasons as previously, the situation is considered only for relatively low adsorption density then;

$$\Omega_m \ll 1, \Omega_- \gg 1, \Omega_+ \gg 1, \Omega_x \ll 1 \quad (7.85)$$

$$[A_z M] = \frac{N_o^z}{\Omega_m^z} \Omega_m \quad (7.86)$$

$$\log D = z \log N_o + z \text{ pH} + \log \frac{K_-^z}{K_m^z} + \frac{ze}{2.3kT} (\psi_o - \psi_{\beta m}) \quad (7.87)$$

$$\frac{d \log D}{d \text{ pH}} = z + \frac{ze}{2.3kT} \frac{d}{d \text{ pH}} (\psi_o - \psi_{\beta m}) \quad (7.88)$$

The two equations that describe the behaviour of the distribution coefficient and the gradient, i.e., (7.87) and (7.88), differ from those for the situation where the surface groups are restricted, (section 7.3.2), only in the term in N_o .

Determination of the independence of the surface groups would require experimentation with varying concentrations of the adsorbent for multivalent ion adsorption. If the relationship between D and N_o was found to be linear then the surface groups would not be free but would cooperate to form a z -dentate ligand. An exponential relationship between D and N_o would indicate that the surface groups were quite independent; a situation perhaps approached with the

adsorption of cations unable to form covalent bonds.

A more precise, but more complex, approach to this problem would consider the probability of finding amongst the complete array of surface groups an arrangement of z of them suitably ionised or ionisable and capable of forming an adsorption site for a z -valent cation.

7.3.4 Adsorption at Low Concentration and Comparison with Experimental Observations

When the hydrous oxide surface is not highly charged and the total concentration of the adsorbing metal cation is low the adsorption isotherm may be described by (7.76) or (7.86) and the slope of the $\log D/pH$ plot will be given by (7.78). This slope is dependent not only upon the ion charge but also upon the differences in the electrical potentials experienced by the adsorbing cation and the ion that it replaces. Because one of these ions is a matrix component, a p.d. ion, it experiences the surface potential ψ_0 , which, using (4.28), can be replaced by a function of the surface charge, σ_0 . (7.87) and (7.78) become;

$$\log D = z \log N_0 + z pH + \log \frac{K_-^z}{K_m} + \frac{4\pi ze\beta_m \sigma_0}{2.3kT\epsilon_m} \quad (7.89)$$

$$\frac{d \log D}{d pH} = z + \frac{4\pi ze\beta_m}{2.3kT\epsilon_m} \frac{d\sigma_0}{d pH} \quad (7.90)$$

where β_m is the distance between the surface and the plane of centres of the adsorbed cation, and ϵ_m is the electrical permittivity of this region. (7.89) with $z = 2$ is essentially the same as equation (9) of Forbes et al.¹⁸⁹ for the adsorption of divalent species by goethite.

The slope of the $\log D/pH$ plots is not simply the ion charge, nor as commonly suggested, equal to the number of protons released

from the surface on adsorption.

In Chapters Four and Five it was seen that for most hydrous oxides $d\sigma_0/d\text{pH}$ is approximately constant with a value dependent upon the electrolyte concentration. Furthermore as pH increases, the surface charge becomes more negative so that $d\sigma_0/d\text{pH} < 0$. Thus $\log D/d\text{pH}$ will be constant but decrease with increasing ionic strength as reported by Kolarik²⁶⁵ and Bonner et al.²⁶⁴ for strontium adsorption onto the hydrous oxides of iron(III), manganese(IV) and aluminium (fig. 7.2).

The parameter β_m may represent the position of the adsorbed ion near the surface¹⁸⁹ or alternatively it is a measure of the difference between the two potentials ψ_0 and $\psi_{\beta m}$, i.e., it is related to the difference between the environments of the two ions in the adsorbed state. For ions that are adsorbed close to the surface $d \log D/d\text{pH}$ will be greater than for those further away, i.e., from (7.90) the difference, $z - (d \log D/d\text{pH})$, for any series of cations adsorbed by the same surface will be a measure of the proximity of each to the surface, or the similarity each bears to the exchanging ion.

For cations that do not enter into covalent bonding with the surface, e.g., non-hydrolysing cations, $d \log D/d\text{pH}$ might decrease with ion size. Kinniburgh et al.¹⁸⁰ studied the adsorption of calcium and strontium onto gibbsite and a hydrous aluminium oxide gel. In each case $d \log D/d\text{pH}$ was less for strontium than for calcium, viz. 0.81 and 0.85 on gibbsite and 0.94 and 1.01 on the gel. Huang and Stumm¹⁷⁹ studied the adsorption of the alkaline earth metal cations onto alumina. From an indirect method, making simple mass action assumptions, they found that the apparent quantity of H^+ released by adsorption increased most rapidly with pH for Mg^{2+} , less for Ca^{2+} and least rapidly for Ba^{2+} ; the reverse of the ion size order. It can be shown from their assumptions that the values of $d \log D/d\text{pH}$ would

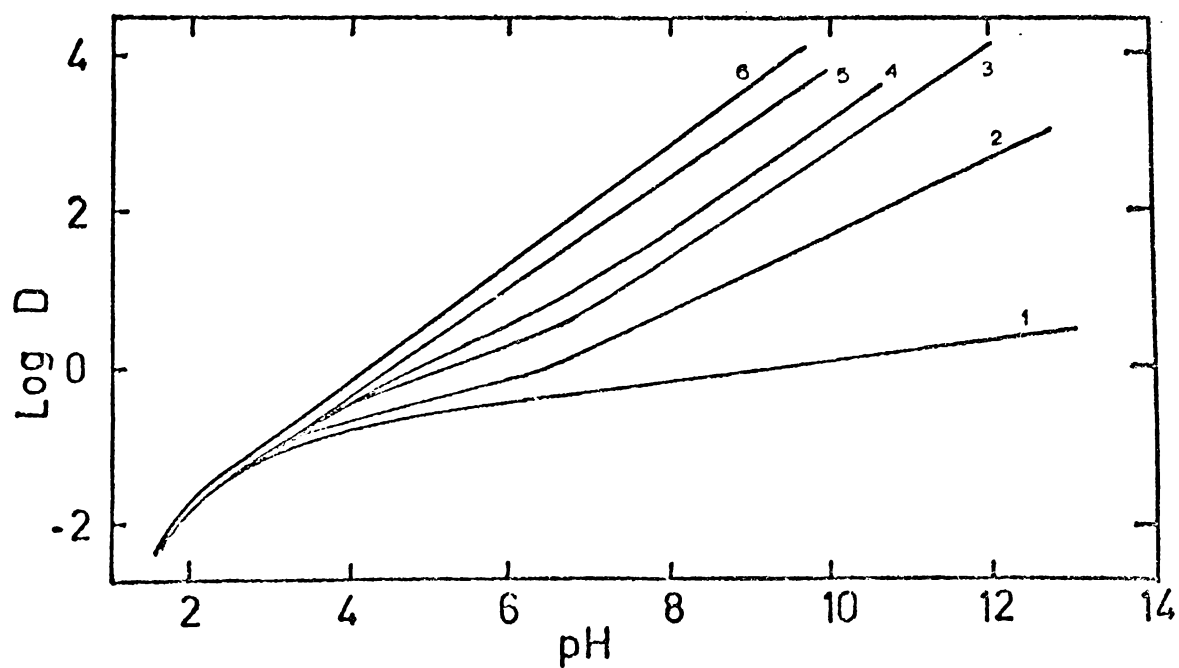


Figure 7.2. The adsorption of strontium by hydrous manganese(IV) oxide. (Redrawn from ref. 265.) Strontium concentrations; 1 5×10^{-2} M; 2, 2×10^{-2} M; 3, 10^{-2} M; 4, 5×10^{-3} M; 5, 10^{-4} M, 6, 10^{-5} M and 10^{-7} M.

decrease in the order: $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$. The Mg^{2+} cation is small and highly charged; it is the ion most like the ion that it replaces, i.e., H^+ . Of all these ions, Mg^{2+} will, on adsorption, experience a potential most like that of a surface component.

A different situation is found for hydrolysable metal cations. Table 7.1 gives the values of β_m , calculated from the data of Forbes *et al.*,¹⁸⁹ for a series of hydrolysable ions adsorbed by goethite. The ionic radii, equilibrium constants for hydrolysis and complex formation with oxalate, and the hydroxide solubility product are also given. β_m correlates better with the ease of hydrolysis (as noted by Forbes *et al.*), oxy-ligand complex formation and hydroxide precipitation than with the ion radius. The apparent closeness of the adsorbed copper ion to the surface was taken to indicate that they were in direct chemical association, i.e., deprotonated surface hydroxyl groups were ligands of the copper ion. The matrix metal cation is completely hydrolysed and so it is not improbable that it might form a bond via an oxygen bridge to a highly hydrolysed adsorbed cation. (It is this type of bond formation that is especially considered to be "specific" and it is the suggested mode of adsorption for many hydrolysable cations onto hydrous metal oxides.) The pH at which 50% of the added cation is adsorbed (pH_{50}) is another indication of its affinity for the surface. The values of this parameter for the five cations studied by Forbes *et al.* have been interpolated from their data and also show the same relation to oxy-ligand formation; copper was the most strongly adsorbed. Because Cu^{2+} and H^+ experienced a similar electrical potential when adsorbed (i.e., $\psi_0 - \psi_{\beta m} \rightarrow 0$) and Cu^{2+} was strongly bound, Forbes *et al.* said the surface showed a "high relative affinity for copper".

As the adsorbing cation becomes more like the matrix metal cation its adsorption becomes more pH dependent and also more intense. The

Table 7.1 Apparent Distance from the Surface of the Plane of Centres of some Cations Adsorbed onto goethite and some properties of these ions. (Taken in part from Forbes et al.,¹⁸⁹ and from Kinniburgh et al.¹⁸⁰)

	X ($\times 10^2$)	n _{app}	β_m 10^{-10} m	r _i 10^{-10} m	p*K ₁	pK _{sp}	-pK ₁ (ox)	pH ₅₀
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
Cu(II)	-0.22	1.66	0.18	0.92	8.0	19.3	5.53	5.25
Pb(II)	-1.06	1.05	0.86	1.17	7.9, 8.8	16.8	3.32	5.7
Zn(II)	-1.15	1.00	0.93	0.69	9.2, 9.0	16.7	3.44	7.1
Co(II)	-1.21	0.86	0.98	0.70	8.9, 9.9	14.8	3.87	7.4
Cd(II)	-1.46	0.69	1.2	0.92	9.0, 10.2	14.1	3.0	7.8
Ca(II)	-	0.95	0.96	0.94	10.3	5.0	1.66	(7.15)
Fe(III)	-	-	-	0.53	2.9	39	7.5	-

(a) Forbes' parameter. (b) apparent slope of log D/pH plot. (c) distance from surface to ion centre (calculated using $\epsilon_m = \epsilon_0 = 15 \cdot \epsilon_{vac}$, as suggested in ref. 109). (d) ionic radius (from ref. 183). (e) - log of first equilibrium constant of hydrolysis (from refs. 189 and 146). (f) - log of hydroxide solubility product (from ref. 146). (g) log of first equilibrium constant for complex formation with oxalate (from ref. 146). (h) pH for 50% of cation to be adsorbed.

limiting case is of course the adsorption of an ion onto its own oxide or hydroxide. In this case $\beta_m = 0$ and $\psi_o = \psi_{\beta_m}$. From (7.90) the slope of the log D/pH plot would be expected to be z . For such a system for small changes the amount of precipitate, $[AM]$, would be constant and so;

$$\frac{d \log D}{d \text{ pH}} = - \frac{d \log [M^{z+}]}{d \text{ pH}} \quad (7.91)$$

For the dissolution or precipitation of aluminium hydrous oxides the slope of the plots of $\log [M^{z+}]$ against pH equal the charge of the dominant ion; at suitably low pH when Al^{3+} is the major solution species $d \log [M^{z+}]/d \text{ pH} = - 3$.^{234, 235}

The values of the parameters for calcium adsorption onto a hydrous iron(III) oxide gel are also reproduced in Table 7.1. These have been determined from the data of Kinniburgh *et al.*,¹⁸⁰ who used an adsorbing medium of quite different concentrations and so direct comparison of the pH_{50} value is not reasonable; if a correction is made for the adsorbent concentration the value would be at somewhat higher concentration but little change would be expected in the slope of the log D/pH plot. From the values of the parameters associated with calcium oxy-ligand formation it is clear that calcium is the least like iron(III) in this respect. However, the apparent slope of the log D/pH plot is greater than for both cobalt and cadmium. This may be associated with the concept that calcium is the cation with the greatest similarity to H^+ .

Silica appears to differ from the more amphoteric hydrous oxides. Allen and Matijević¹⁹¹ found slopes of the log D/pH plots approached the ion charge, i.e., the adsorbing ion occupied a site very much like the p.d. ion it replaced. In this case if (4.24) holds β_m must be very small. In their double layer calculations Yates *et al.*²⁶⁷ also found

that for a silica-type system β needed to be very small. They said further that their system, designed as a test of the porous double layer model in which the outer layers of the solid are a porous gel matrix,²⁶⁹ could not differentiate between the rigid surface and the gel layer concepts. However for the more amphoteric oxides there is quite definitely a difference in the positions of adsorption of cations and p.d. ions and so it is unlikely that they have a porous nature; the same may not be said for silica. Similar conclusions have been reached by other workers using different techniques.²⁷⁰ At the silica surface it was suggested that a gel layer of incompletely condensed polysilicic acid occurred. The ion adsorption properties of this material can then be adequately described by the mass action model as used by Allen *et al.*²⁶⁸

For the adsorption of any simple metal cation from dilute solution onto a hydrous oxide the difference between the ion charge and the slope of the log D/pH plot will indicate the similarity between the adsorbing cation and the matrix components, i.e., either the metal cation or H^+ . For non-hydrolysed ions this will be the similarity induced by the size of the ion and the concentration of charge. Small charged species such as H^+ , Li^+ , Na^+ and Mg^{2+} are all strongly hydrated and induce considerable structuring in the water close to them, but larger more diffuse ions such as K^+ and Sr^{2+} are much less effective in this respect. Thus the log D/pH plot is steeper for Ca^{2+} adsorption than for Sr^{2+} and it would be anticipated that the respective plot would be steeper for Na^+ adsorption than for either K^+ or Tl^+ . If the cation can be involved in some form of covalent bonding to the matrix then the difference referred to above will be reduced until it is zero whereupon the bond between the cation and the surface will be as covalent as the O - H or the O - (matrix cation) bond.

7.3.5 Adsorption from a Mixture and Ion Selectivity

An effect that has not generally been considered, but may be important to cation adsorption under some conditions, is the influence of the presence of other adsorbing cations. In particular, the adsorption of many divalent cations by hydrous oxides¹⁸⁰ has been studied from relatively concentrated solutions of simple sodium salts (e.g., refs. 104, 179, 180, 185, 206, 264, 265). The high concentration of these salts maintains a constant ionic strength so that ion activities do not change. It has also been suggested that the high concentration of weakly adsorbing sodium would ensure that it occupied all "non-specific" adsorption sites. Divalent cation adsorption would then proceed only at "specific" sites.¹⁸⁰ However no good evidence for the existence of two adsorption sites on simple hydrous metal oxides has been presented; e.g., adsorption isotherms of the form of figure 1 of Allen et al.²⁶⁸ Nevertheless the sodium would dominate the adsorption of cations in the diffuse layer because of its very high relative concentration; divalent cation adsorption in this region would be insignificant.

The aim of this section was to find, by investigating the adsorption behaviour of two cations from a mixture of their salts of an indifferent anion, the effects to be expected when two cations are being adsorbed. To do this it became necessary to find the properties and conditions that may influence the selection of one cation at the expense of the other.

The system under consideration here will be two z -valent cations, L^{z+} and M^{z+} , which may both adsorb from a solution of an indifferent anion onto a hydrous oxide. This may arrange all its surface hydroxyl groups, HA , into potential adsorption sites, H_zA_z . The surface ionisation processes are represented by (7.46) to (7.51). In addition to the adsorption process for cation M^{z+} given in (7.57)

there is a similar process for the adsorption of the cation L^{z+} to form an adsorption complex $A_z L$;



At equilibrium for this process;

$$[A_z L] = [A_z^{2-}] \Omega_\ell ; \quad \Omega_\ell = \frac{[L^{z+}]}{K_\ell} \exp\left(-\frac{ze}{kT} \psi_{\beta\ell}\right) \quad (7.93)$$

where K_ℓ is the dissociation constant for the adsorption complex $A_z L$, defined in a manner similar to K_m , (7.69), and $\psi_{\beta\ell}$ is the potential difference between the bulk solution and the plane of centres of adsorbed cations L^{z+} , a distance β_ℓ from the surface proper. If the surface protonation and anion adsorption reactions can be neglected then the total concentration of surface groups is given by;

$$\frac{N_O}{z} = [A_z M] + [A_z L] + \sum_{i=0}^z [H_i A_z^{i-}] \quad (7.94)$$

$$= [A_z M] \left(1 + \frac{1}{\Omega_m} + \frac{\Omega_\ell}{\Omega_m} + \frac{\Omega_-}{\Omega_m} (1 + \Omega_- (1 + \dots + \Omega_-^z))\right) \quad (7.95)$$

The concentrations of the adsorbed cations are;

$$[A_z M] = \frac{N_O}{z} / \left(1 + \frac{\Omega_\ell}{\Omega_m} + \frac{1}{\Omega_m} + \frac{\Omega_-}{\Omega_m} \cdot \frac{\Omega_-^z - 1}{\Omega_- - 1}\right) \quad (7.96)$$

$$[A_z L] = \frac{N_O}{z} / \left(1 + \frac{\Omega_m}{\Omega_\ell} + \frac{1}{\Omega_\ell} + \frac{\Omega_-}{\Omega_\ell} \cdot \frac{\Omega_-^z - 1}{\Omega_- - 1}\right) \quad (7.97)$$

At low concentrations of both cations and pH near the PZC then;

$$\Omega_m \ll 1, \Omega_\ell \ll 1, \Omega_- \gg 1 \quad (7.98)$$

$$[A_z M] = \frac{N_o \Omega_m}{z \Omega_-^z} = \frac{N_o [M^{z+}] K_-^z}{z [H^+] K_m} \exp\left(\frac{ze}{kT} (\psi_o - \psi_{\beta m})\right) \quad (7.99)$$

$$[A_z L] = \frac{N_o \Omega_\ell}{z \Omega_-^z} = \frac{N_o [L^{z+}] K_-^z}{z [H^+] K_\ell} \exp\left(\frac{ze}{kT} (\psi_o - \psi_{\beta \ell})\right) \quad (7.100)$$

These equations are the same as (7.76) which describes the adsorption of a single cation under the same conditions. Thus at suitably low pH and cation concentration the adsorptions are independent except for any influences caused via the surface charge.

A parameter used to describe the selectivity preference shown by an ion exchanger for a pair of adsorbing or exchanging ions is the selectivity coefficient, K_2^1 , defined by;

$$K_2^1 = \frac{[\text{species 1}]_{\text{solid}}^{z_2} [\text{species 2}]_{\text{solution}}^{z_1}}{[\text{species 2}]_{\text{solid}}^{z_1} [\text{species 1}]_{\text{solution}}^{z_2}} \quad (7.101)$$

$$= \frac{D_1^{z_2}}{D_2^{z_1}} \quad (7.102)$$

where z_i is the charge of species i . (Concentrations have been used again here in lieu of activities.) Remembering that $D_m = [A_z M]/[M^{z+}]$ and $D_\ell = [A_z L]/[L^{z+}]$ allows the selectivity coefficient for this system to be determined from (7.99 and (7.100).

$$K_m^\ell = \frac{K_m}{K_\ell} \exp\left(\frac{ze}{kT} (\psi_{\beta m} - \psi_{\beta \ell})\right) \quad (7.103)$$

$$= \frac{K_m}{K_\ell} \exp\left(\frac{4\pi ze}{kT} \left(\frac{\beta_m}{\epsilon_m} - \frac{\beta_\ell}{\epsilon_\ell}\right) \sigma_o\right) \quad (7.104)$$

where the function in the surface charge, σ_o , has been obtained from

(4.24). As σ_0 is a function of pH it is seen that the selectivity will change with pH. In particular it is seen that if K_ℓ and K_m are not greatly different then there will be a reversal in the preference of the surface near the PZC, the pH at which σ_0 changes from positive to negative. The preferred ion at low pH will be the one with the larger value of β , i.e., if $\beta_m > \beta_\ell$, $K_m^\ell < 1$ and so the ion which lies further from the surface, M^{z+} , will be the more strongly adsorbed (fig. 7.3). Such an ion would be expected to have a low tendency to engage in covalent bonding with the matrix and would have a greater ionic radius; it would be more polarisable. It is predicted that such ions as K^+ and Rb^+ will adsorb more strongly at low pH than those ions with similar characteristics to the matrix of components. With an increase in pH, as the surface negative charge increases, these large diffuse ions (K^+ and Rb^+) will lose favour to the small ions or those able to enter into covalent bonding with the surface. On this basis some of the selectivity changes described in section 6.3.1 can be understood.

The second case of interest occurs at high pH, when there is sufficient of one cation to saturate the surface but the adsorption of the other cation is relatively low. In this situation;

$$\Omega_m \gg 1, \Omega_\ell \ll 1, \Omega_- \ll 1 \quad (7.105)$$

and so from (7.96) and (7.97);

$$[A_z M] = \frac{N_O}{z} \quad (7.106)$$

$$[A_z L] = \frac{N_O \Omega_\ell}{z \Omega_m} = \frac{N_O K_m [L^{z+}]}{z K_\ell [M^{z+}]} \exp\left(\frac{ze}{kT} (\psi_{\beta m} - \psi_{\beta \ell})\right) \quad (7.107)$$

From (7.106) the differential of $\log D_m$ with respect to pH will

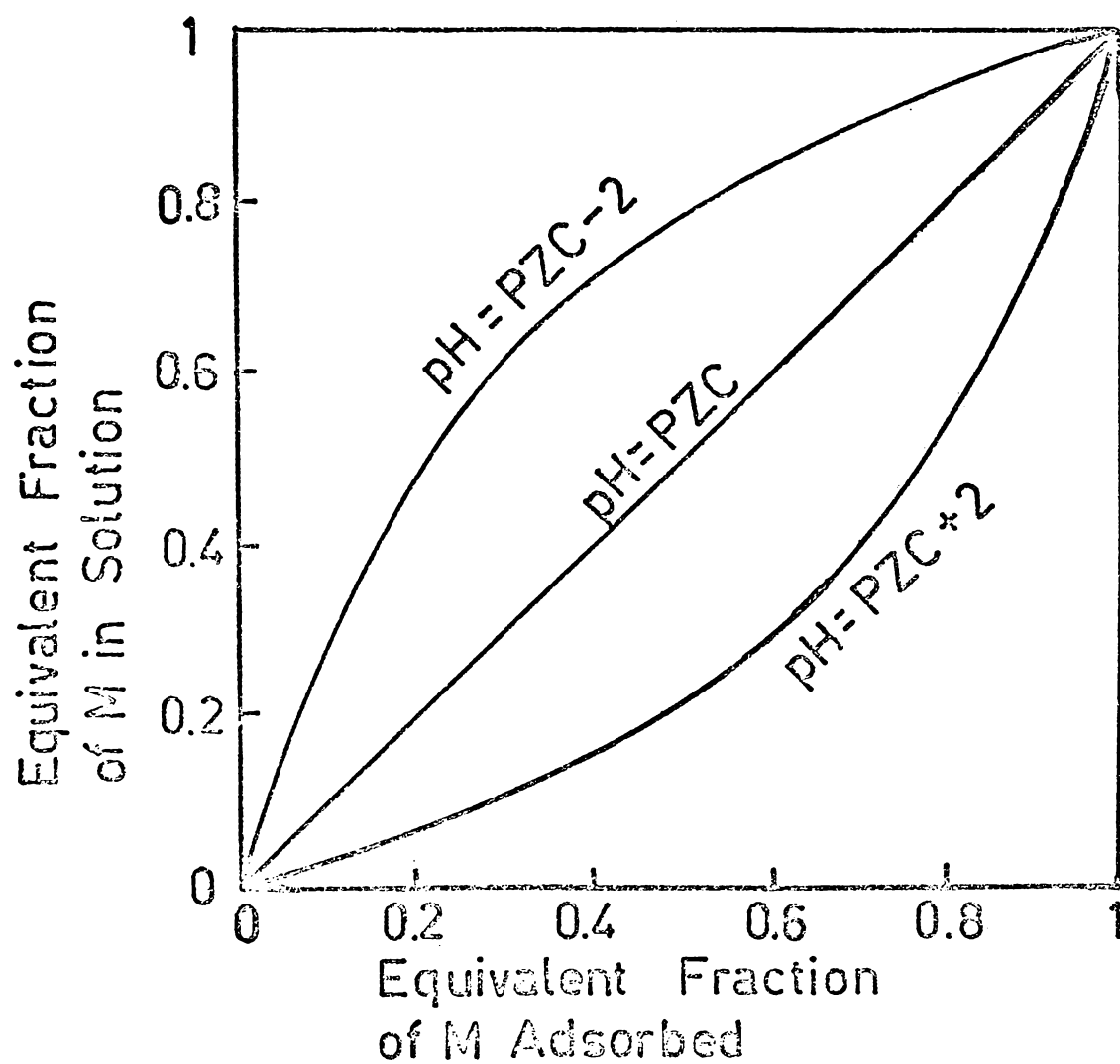


Figure 7.3. A representation of the ion exchange equilibrium between two cations, M^+ and L^+ , which differ only in that $\beta_m \gg \beta_l$.

be zero whilst that for $\log D_\ell$ is given by;

$$\frac{d \log D_\ell}{d \text{ pH}} = \frac{ze}{2.3kT} \frac{d}{d \text{ pH}} (\psi_{\beta m} - \psi_{\beta \ell}) \quad (7.108)$$

The adsorption of the minor cation will depend upon the similarity it bears to the dominant cation. If they appear identical it will not be further adsorbed, nor will it exchange off; this is the expected situation with isotopic exchange where there is no significant ionic difference between the cations and so after equilibrium is attained the ratio will be constant in both states. However, if one cation can apparently lie closer to the surface than the other it will adsorb more strongly as pH is increased, at the expense of the other. Again this is reflected in the selectivity coefficient which from (7.106) and (7.107) it can be seen has not changed from the expression (7.104).

The preference shown by a hydrous oxide for one or other of a pair of equi-valent cations will be dependent upon the relative similarity of these ions to the matrix components. The cations least like the matrix components, large polarisable non-hydrolysable ions, will be the more favoured at low pH. With pH increase, however, although the surface will bind these ions more readily, the relative increase noted will be greater for ions that show more similarity to the matrix components, i.e., those like H^+ or the matrix metal cation.

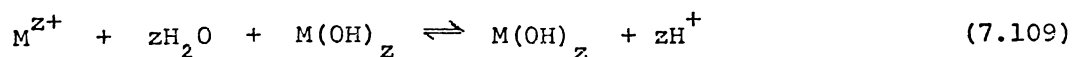
At low surface occupancy as the distribution coefficient is roughly constant selectivity will not change with the concentration of the two cations. When saturation is approached, however, the distribution coefficient for each cation becomes a function of its total added concentration. Therefore, from (7.102), the selectivity coefficient will also vary with the total cation concentrations.

Where the adsorption of a cation is being studied from an aqueous solution containing the salts of other cations, the adsorption of all cations should be understood before mechanistic discussions are made. This is particularly important if surface saturation was being approached. In such a situation competition for adsorption sites would be expected. The extent of the adsorption of any species would depend upon the natures and concentrations of all cations present, and the pH.

7.3.6 Adsorption of the Cation of a Slightly Soluble Hydroxide

In many soil clays, such as those containing allophane, both aluminosilicates and the slightly soluble hydroxides of metals, such as iron and aluminium, are found together. The manner in which the metal cation might be adsorbed by a hydrous oxide-like aluminosilicate is of interest.

Consider an aqueous suspension of a slightly soluble metal hydroxide, $M(OH)_z$, at a pH below its point of minimum solubility and another hydrous oxide of a different nature with cation adsorption sites zAH . The cation M^{z+} will then be distributed between the three phases according to the following equilibria;



The first equilibrium is written in this manner as adsorption of the cation leaves the surface of the hydroxide in the same state. Again A_zM is an interfacial ion "pair". If there is a suitably large concentration of the hydroxide present this will control the concentration of the cation, which will then be given by;

$$K_{so} = [M^{z+}] [OH^-]^z \quad (7.111)$$

K_{so} is the solubility product of the hydroxide. The concentration of the adsorbed species, $[A_z M]$, can be obtained from (7.86), which, incorporating (7.111), becomes;

$$[A_z M] = \frac{N_o^z \Omega_m}{\Omega_-^z} \frac{K_{so}}{[OH^-]^z} \quad (7.112)$$

$$= \frac{K_{so} K_-^z}{K_m} \frac{N_o^z}{[OH^-]^z [H^+]^z} \exp \left(\frac{ze}{kT} (\psi_o - \psi_{\beta m}) \right) \quad (7.113)$$

$$\therefore \log [A_z M] = z \log N_o + \text{constant} + \frac{ze}{2.3kT} (\psi_o - \psi_{\beta m}) \quad (7.114)$$

Differentiating this with respect to pH gives;

$$\frac{d \log [A_z M]}{d \text{pH}} = \frac{ze}{2.3kT} \frac{d}{d \text{pH}} (\psi_o - \psi_{\beta m}) \quad (7.115)$$

The derivative of the difference in potentials is negative and so the actual amount of the cation adsorbed onto the hydrous oxide (not the hydroxide) will actually decrease with increasing pH. At the same time the cation is transferred to the hydroxide phase. Furthermore as the derivative of the differences in potentials is constant, the logarithm of the concentration of the adsorbed species, $\log [A_z M]$, will vary linearly with pH for low adsorption.

A system which displayed these general characteristics was studied by Turner and Brydon.⁷⁶ They prepared montmorillonites in the aluminium form at low pH. When the pH was increased the equilibrium aluminium concentration was observed to be in excess of the solubility product of gibbsite. If the amount of adsorbed

aluminium exceeded a definite value gibbsite then formed spontaneously and the aluminium transferred from the clay to the gibbsite. For clay suspensions with a lower content of adsorbed aluminium the same end result was obtained if a gibbsite seed was added.

7.3.7 Adsorption of a Cation in the Presence of Another Hydroxide

The final situation to be considered here is the influence that the presence of a slightly soluble hydroxide, itself not adsorbing any other cationic species, can have on the adsorption of a second cation by a hydrous oxide surface. In this case the hydroxide will be $M(OH)_z$ and the adsorbing cation will be monovalent L^+ . It is assumed that the anion present has no active rôle in this system.

The pertinent equilibrium reactions include the dissolution-formation reactions of the hydroxide, (7.109), and the adsorption reactions of the cations M^{z+} , (7.110), and of L^+ , which is;



If the equilibrium constant for the formation of the interfacial ion pair, AL , is K_ℓ , then in a manner similar to that used previously (e.g., equations (7.13), (7.17) and (7.21), the distribution of L^+ between the two states is given by;

$$[AL] = [A^-] \Omega_\ell ; \quad \Omega_\ell = \frac{[L^+]}{K_\ell} \exp\left(-\frac{e}{kT} \psi_{\beta\ell}\right) \quad (7.117)$$

$\psi_{\beta\ell}$ is the apparent potential difference between the plane of centres of adsorbed cation, L^+ , and the bulk solution.

All the surface hydroxyl groups will be distributed between four states, thus;

$$N_O = z[A_z M] + [AL] + [AH] + [A^-] \quad (7.118)$$

From (7.19), (7.82 and (7.122);

$$N_o = z \frac{[AL]^z}{\Omega_\ell^z} \Omega_m + [AL] \left(1 + \frac{1}{\Omega_\ell} + \frac{\Omega_-}{\Omega_\ell}\right) \quad (7.119)$$

There are two situations of particular interest here. First, when the cation from the hydroxide does not adsorb sufficiently to occupy many adsorption sites the adsorption behaviour of L^+ will be the same as that described for M^+ in section 7.3.1. This will occur if there is only a little hydroxide, if the pH is too high for much dissolution or the concentration of L^+ is high. However at lower pH, when Ω_m is large, i.e., both the concentration of the cation from the hydroxide in the solution and its tendency to adsorb are sufficiently large so that M^{z+} occupies a significant part of the adsorption sites, then;

$$N_o = z \frac{[AL]^z}{\Omega_\ell^z} \Omega_m \quad (7.120)$$

$$\therefore \frac{[AL]^z}{[L^+]^z} = \frac{N_o K_m}{z K_\ell^z [M^{z+}]} \exp\left(\frac{ze}{kT} (\psi_{\beta m} - \psi_{\beta \ell})\right) \quad (7.121)$$

But $[AL]/[L^+] = D_\ell$, the distribution coefficient, and $[M^{z+}]$ is given by (7.111), therefore;

$$D_\ell = \frac{N_o K_m [OH^-]^z}{z K_\ell K_{so}} \exp\left(\frac{ze}{kT} (\psi_{\beta m} - \psi_{\beta \ell})\right) \quad (7.122)$$

$$\text{i.e. } \log D_\ell = \frac{1}{z} \log N_o/z + \text{constant} + \text{pH} + \frac{e}{2.3kT} (\psi_{\beta m} - \psi_{\beta \ell}) \quad (7.123)$$

Upon differentiating with respect to pH this yields;

$$\frac{d \log D_\ell}{d \text{pH}} = 1 + \frac{e}{2.3kT} \frac{d}{d \text{pH}} (\psi_{\beta m} - \psi_{\beta \ell}) \quad (7.124)$$

As the difference in the potentials $\psi_o - \psi_{\beta m}$ varies linearly with pH so too will the difference $\psi_{\beta l} - \psi_{\beta m}$. However as both M^{z+} and L^+ when adsorbed, occupy positions not actually at the surface but some short distance away, then $\psi_{\beta m} - \psi_{\beta l}$ will be smaller than $\psi_o - \psi_{\beta l}$. Thus the slope of the log D/pH plot for the cation that does not belong to the hydroxide will be steeper when the hydroxide cation is present, and adsorbing strongly, than when it is absent or its concentration is too small to occupy a significant number of surface sites.

Furthermore, if the surface was saturated, from (7.119) an increase in the concentration of L^+ would reduce the pH at which interference from the hydroxide cation adsorption affected log D_l . There would be no change if the surface was not saturated, or approaching that state.

7.3.8 Summary of the Proposed Electrochemical Theory

The site-binding model²⁶⁷ of the electrochemical double layer at the hydrous oxide/aqueous interface assumes that ion adsorption proceeds at charged surface sites formed by the adsorption or desorption of the p.d. ions, H^+ and OH^- . The model also assumes, with justification, that the adsorption occurs predominantly at the inner Helmholtz plane, close to the surface, and not in the diffuse layer. The nett adsorption process is an exchange of ions from the solution for p.d. ions of the surface to form interfacial ion-pairs.

From this model the distribution of a simple cation between the surface of a hydrous oxide and an aqueous solution can be described by the following equation;

$$\log D = \log\{f(N_o, z)\} + \log \frac{K_z^-}{K_m} + zpH + \frac{ze}{2.3kT} (\psi_o - \psi_{\beta m}) \quad (7.125)$$

Thus the amount of the cation adsorbed will be determined by the following parameters:

- (i) the pH,
- (ii) the cation charge (z),
- (iii) the cation concentration,
- (iv) the concentration of suitable adsorption sites (N_o),
- (v) the equilibrium constant for the formation of the interfacial ion pair (K_m),
- (vi) the dissociation constant of the neutral surface hydroxyl groups (K_-),
- (vii) the difference between the electrical potentials experienced by the exchanging ions in their adsorbed states ($\psi_o - \psi_{\beta m}$).

The degree of saturation of the surface, and the presence of competing ions, will also be influential.

For low site occupancy the first term in (7.125), $\log f(N_o, z)$, would be constant and, if the last term can be related to the surface charge, $\log D$ would be linear with pH.

Specific adsorption effects, such as covalent bond formation with the surface, are included in the equilibrium constant for the formation of the ion pair, i.e., K_m . The degree of pH dependence is related to the ion charge and the term involving the difference in the electrical potentials experienced in the adsorbed state. As this term may be expressed as a function of the surface charge, the distance from the ion centre to the surface and the dielectric constant of the solid, surface properties and the concentration of the electrolyte in the solution are important. Ions that are adsorbed a larger distance from the surface would not experience electrical influences as strong as those felt by closely bound cations and their adsorption would be less variable with pH. Such ions would be large

with only a low charge. Small ions with high charge density or ions capable of forming covalent bonds with the hydrous oxide (generally easily hydrolysed species) would be more strongly influenced by pH changes. In the adsorbed state they would experience a potential similar to that experienced by adsorbed H^+ or matrix metal cation. A result of the differing influence of pH would be changes in the selectivity, shown by the surface for various cations, with pH. Selectivity may also vary with the total cation concentrations.

All the phenomena that influence cation adsorption by hydrous oxides that were summarised in section 6.3.7 are included in the site-binding model.

The predictions made above have all been substantiated by experimental observations recorded in the literature and a number of observed adsorption phenomena have been explained. The simple mass action approach was seen to be a special case of this model, namely, when the electrical potential difference term is reduced to zero.

In section 7.3.1 it was shown that at low site occupancy $\log D$ is independent of the total concentration of the adsorbing cation, except in the manner that it influences the surface charge of the various potentials. When a state of surface saturation is approached, or attained, increasing the total concentration of the adsorbing cation will substantially reduce its distribution coefficient.

The model further predicts the adsorption of the cation of a slightly soluble hydroxide by another hydrous oxide. With decreasing pH, below its point of minimum solubility, the hydroxide will be dissolved and the released cation will adsorb onto the hydrous oxide. This may result in the saturation of the available sites and then displacement of other adsorbed cations from them. With an increase in pH there would be a transfer of the cation back to the hydroxide.

A major difference exists between cation adsorption by

precipitated silica and the other hydrous oxides. Only with this type of silica do non-matrix cations appear to occupy the same position in the adsorbed state as H^+ , the cation being replaced. It has been suggested that the silica/aqueous interface is porous; it has a gel layer of incompletely condensed polysilicic acid. (The other hydrous oxides have discrete surfaces.) In the adsorbed state within this gel layer both H^+ and the adsorbed cation would experience essentially the same electrical potential; an electrochemical distinction would be difficult and has not been observed.

7.4 Conclusion

An electrochemical model has been proposed to explain the adsorption of cations by hydrous oxides.

This model is based on properties of both the cation and the surface and the interactions of the surface with potential determining ions.

It gives a sound electrochemical basis for the variation of adsorption dependence on pH shown by different cations, for selectivity, for selectivity variations, and for the influences of other cations.

This model also explains many of the observations of cation adsorption by hydrous oxides found in the literature.

CHAPTER EIGHT

CATION ADSORPTION BY ALLOPHANE:

AN EXPERIMENTAL STUDY

8.1 Introduction

In the previous chapter it was noted that some aspects of the interactions of allophane with cations in dilute aqueous solution were not well understood. To clarify this situation an experimental investigation of the adsorption of a number of different cations was instigated. The results obtained were interpreted with the assistance of the theoretical model developed in the previous chapter.

The cations studied were chosen for the following reasons. Sodium is commonly used as a background electrolyte. In this rôle the actual extent of its own adsorption should be known. Potassium is an important nutrient and its behaviour in the soil is dependent upon its adsorption by soil colloids. Calcium is another major soil water cation; it is also commonly used as a soil conditioner and road foundation stabilisation agent. Strontium was studied because of its greater analytical sensitivity, its absence in solutions associated with the clay and because it is not readily hydrolysed. Lead and thallium are both toxic heavy metals, the first is also readily hydrolysed. Finally cobalt is an important trace element in soils; it hydrolyses less readily than lead but more than strontium and calcium.

In addition to the Ohaupo allophane, with which the greater part of the experiment was done, Tirau allophane and Mangawara halloysite were also investigated. The influence of acidification upon the stability of the aluminium, calcium and iron(III) of these clays was also observed.

8.2 Materials and Methods

The clays used were each prepared from a single preparation (see section 3.2) and were in the sodium form. Ohaupo allophane was also treated with acid, either with 0.1 M hydrochloric acid or at pH 3.0 with dilute hydrochloric acid, twice for 20 minutes and then overnight to produce acid-form or hydrogen-form (H-form) respectively. No iron(III) was found in the supernatant after the pH 3.0 washing, even using potassium thiocyanate as indicator, although it was present in the liquors from the 0.1 M acid treatment. All samples were then washed at least 6 times with twice-distilled water over three days before being suspended in twice-distilled water to form a suspension of the required concentration (about 10 g l^{-1}). They were then "aged" for at least one week. All chemicals used were analytical grade and solutions were all prepared in twice-distilled water.

For adsorption experiments suitable known aliquots of clay suspension, electrolyte and dilute acid or base were made up to the required volume and mixed in plastic centrifuge tubes for half an hour. An aliquot of the cation chloride solution was added, the tube was stoppered and mixed for 16 hours by end-over-end rotation at 15 rpm at 20°C . The pH of the suspension was then recorded (except in the case when potassium was being studied in which case a separate sample was removed for this determination to prevent contamination from the KCl salt bridge of the calomel electrode), and the tube was centrifuged at 3000 rpm in a MSE Multex centrifuge for 10 minutes. The supernatant was decanted off. If this was not free of clay it was further centrifuged at high speed (in a Sorvall RC2-B centrifuge) at 17,000 rpm for 20 minutes.

The liquid phase was analysed for the cation. Sodium was determined by flame photometry; potassium and strontium by flame emission; calcium, cobalt, lead and aluminium by atomic adsorption (for

a discussion of some interferences found using AA see Appendix IV); iron and aluminium spectrophotometrically, iron with o-phenanthroline (using the method described by Vogel,⁷⁴ p. 787) and aluminium with solochrome cyanine R.¹⁴⁵ Thallium was determined by following the isotope Tl-204, a beta emitter, which had been added to a thallium solution in trace quantities.

8.3 Results and Discussions

8.3.1 Extraction of Aluminium by Acidification

The concentration of aluminium found in suspensions of the three clays in their sodium forms is plotted against the final suspension pH in figure 8.1. This has also been done for the H-form of the Ohaupo allophane. The range of measurements was limited as the solubility was not investigated above pH 8 and concentrations less than 10^{-6} M could not be detected with the methods employed. The solid lines are the maximum concentrations of monomeric aluminium species in equilibrium with (a) freshly precipitated aluminium hydroxide gel and (b) precipitated gibbsite.²⁷¹

With all clays the extraction of aluminium increased with acidification. Increasing the ionic strength by raising the concentration of sodium chloride in the extracting solution increased the dissolution to only a small extent. The halloysitic clay released the least aluminium whilst the Tirau allophane contained the most soluble material. In the range pH 4 to 6 it produced a solution of the same concentration as that found with amorphous aluminium hydroxide precipitates. The slope of the plot for this allophane also approached the charge of the major aluminium species in the solution, i.e., AlOH^{2+} and Al^{3+} , depending upon the pH. At pH 3.4 the dissolved aluminium accounted for more than 1% of the total weight of clay, 10% of the total aluminium and nearly 40% of the oxalate extractable

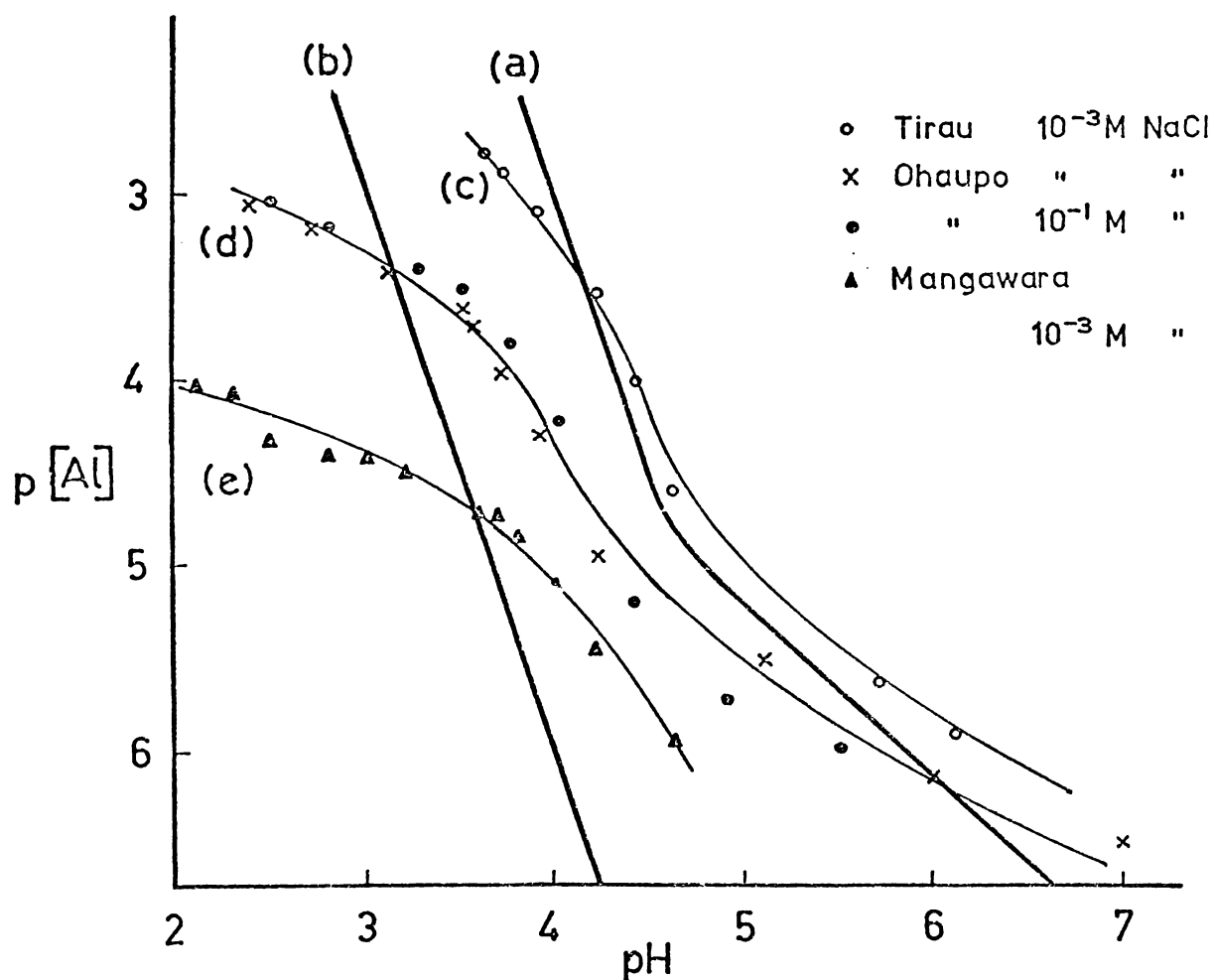


Figure 8.1. Total concentration of monomeric aluminium species (Al^{3+} and $Al(OH)_2^+$) in equilibrium with (a) amorphous aluminium hydroxide and (b) precipitated gibbsite. (From ref. 235.) Also, the concentrations of aluminium found in extracts of Tirau (c), Ohaupo (d) and Mangawara (e) clays.

(labile) aluminium.¹⁸ The ion product $[Al^{3+}] [OH^-]^3$, between pH 3.5 and 5, had a mean value of $10^{-33.0 \pm 0.2}$. The acid extraction of Ohaupo allophane produced lower amounts of aluminium and was less dependent upon the pH. The maximum concentration of aluminium found here, at pH 2.4, corresponded to less than 1% of the sample initial weight; at pH 3.4 it was less than 0.2%.

If on adsorption a cation becomes an integral part of the surface of the adsorbent the plot of the logarithm of its distribution coefficient against pH will have a gradient equal to the charge of the major adsorbing species. When most of the cation is in the adsorbed state the distribution coefficient can be replaced by the solution concentration (see section 7.3.4). For non-porous interfaces this generally implies the solid phase is a hydrous oxide of the cation. If the slope of this plot becomes less than the ion charge the solid is no longer like an infinite matrix of the hydrous oxide. It is becoming, instead, like a weak acid ion exchange material in which the cation on adsorption occupies a position which is on but not a part of the surface.

From the concentration of free aluminium, and the slopes of the plots in figure 8.1, it can be seen that the soluble aluminium in Tirau allophane is in a state comparable to a separate phase of aluminium hydroxide. That this phase is not in a discrete crystalline form, such as gibbsite, was shown in Chapter Three, viz., if any crystalline bodies were present they were not large enough to be observed by XRD; neither was there sufficient crystalline material present in such a phase to give peaks in the DTA curves; furthermore no crystalline bodies were observed by electron microscopy.

The aluminium occurring with the Ohaupo allophane was less soluble than that of the Tirau clay. It is probable that in the Ohaupo clay the soluble aluminium would still be in a phase approaching

free hydrous oxide, or hydroxide, but influenced by some other system. Thus it may be polymeric aluminium hydroxide but it should not be considered to be an infinite matrix; rather it is present as discrete bodies of limited extent; perhaps closely associated with the aluminosilicate matrix which has different charge properties.

The soluble aluminium found for these allophanes was in a form similar to that proposed for allophanes and synthetic aluminosilicates by Cloos *et al.*³⁷ and de Villiers and Jackson,²⁴⁴ i.e., small discrete units of amorphous aluminium hydroxide or hydrous oxides of variable extent.

As much less aluminium was extracted from the halloysite it is unlikely that it contained significant quantities of polymeric aluminium hydrous oxides. It did have more free aluminium than a kaolinite which, under similar circumstances and above pH 3, did not release a detectable quantity to the equilibrating solution.¹³⁵ In this halloysite, aluminium is then found not only as part of the aluminosilicate matrix but also, because of its relatively high lability, as a part of the amorphous material or in a surface-bound and available state.

That the aluminium in allophane can exist in such a highly soluble form for some thousands of years without being transformed into more stable and less soluble crystalline hydroxides, such as gibbsite, is of interest and is discussed below.

The nature of aluminium adsorbed by montmorillonite has been studied by Turner, Brydon and co-workers (ref. 76 and further refs. therein). They found that with the addition of less than 270 mmole per 100 g clay the aluminium entered the montmorillonite interlayers and it maintained an ion product, $[(Al)(OH)^3]$, in solution of near $10^{-33.0}$ (the same as that found here for Tirau allophane). This is much greater than the solubility product of gibbsite ($10^{-36.3}$) but it

is the same as that for amorphous aluminium hydroxide.^{235,271} This concentration of aluminium was not sufficient to initiate the crystallisation of gibbsite. However, if a gibbsite "seed" was added the aluminium transferred from the montmorillonite to the crystalline hydroxide. Turner *et al.* also showed that if a greater amount of aluminium than 270 mmol was added per 100 g clay upon pH increase gibbsite formed spontaneously and the aluminium was removed from the gibbsite without seeding.

Such a situation may occur in allophane soils. In some of these, particularly those with high aluminium contents, gibbsite may be found but in others it is not.¹⁸ During the initial weathering of tephra the dissolution of the various constituents takes place with subsequent deposition and clay mineral formation. It is likely that if there is less than a critical amount of labile aluminium present the aluminium will be incorporated into aluminosilicates and deposited, or adsorbed, on these minerals. Where the concentration is excessive gibbsite will form. Thus although solutions in contact with Tirau allophane are supersaturated with respect to gibbsite unless they are seeded with gibbsite they will remain as they are; in equilibrium with amorphous aluminium hydroxide.

Separation of allophanic clays from soils has been carried out by dispersion not only near pH 9, as used in this study, but also at pH 3.^{14,30} It can be seen that suspension of allophane at this pH will bring about a loss of aluminium. This effect should be considered if acid dispersion is being utilised. Dispersion is more commonly carried out at pH 9. Aluminium loss would be less significant at this pH.

8.3.2 Extraction of Iron by Acidification

The dissolution of iron species from the Ohaupo allophane by acidified 10^{-3} M sodium chloride is shown in figure 8.2. The ordinate

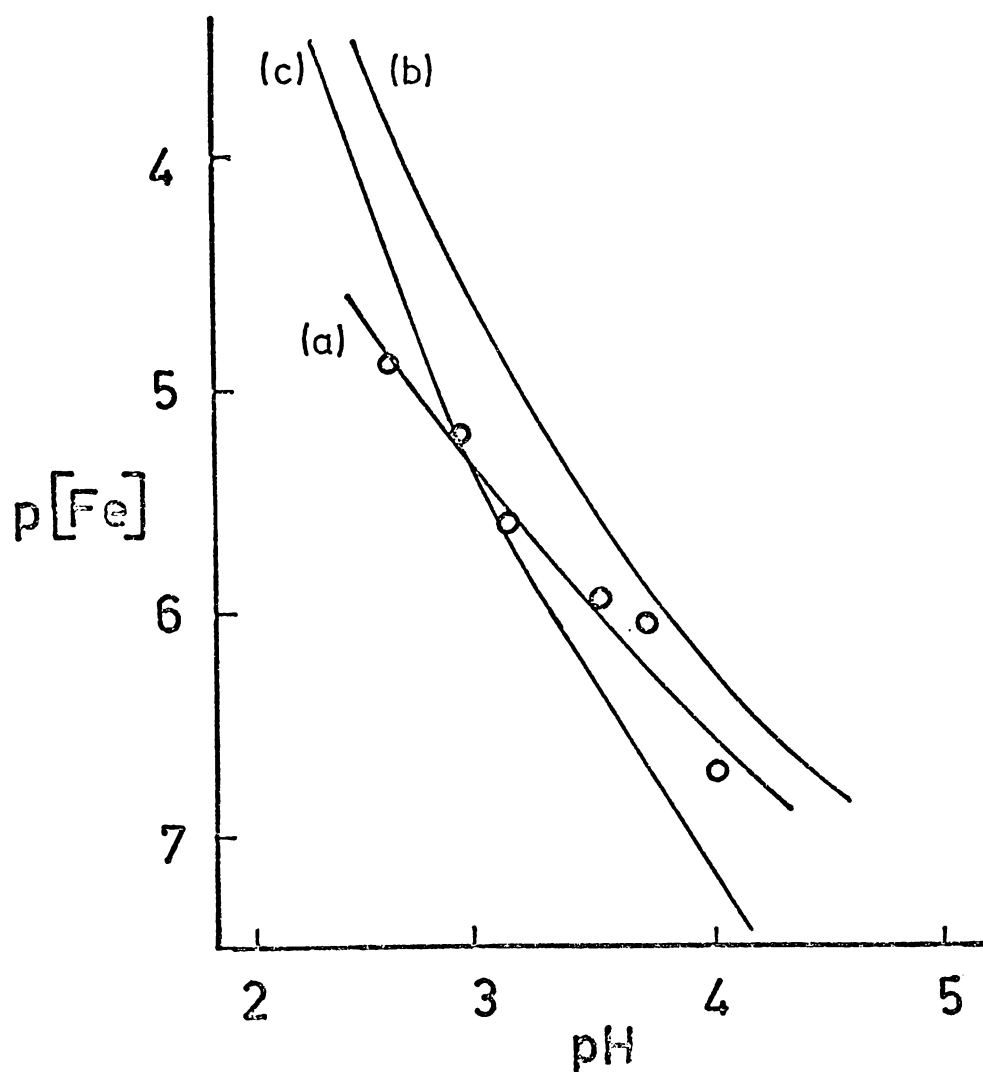


Figure. 8.2. (a) Solubility of iron from Ohaupo clay in 10^{-3}M NaCl at various pH. (b) Solubility of iron(III) precipitated on kaolinite in 0.15 M NaCl. (From ref. 242.) (c) Total concentration monomeric iron(III) species in equilibrium with fresh iron(III) hydroxide precipitate. (From ref. 146.)

is again logarithmic. The amount dissolved at pH greater than 4 was too small to be determined directly and so this region was neglected. Included in figure 8.2 is the solubility of iron(III) in 0.15 M sodium chloride ²⁷² and also the concentrations of the monomeric iron(III) hydroxyl species calculated from the equilibrium constants for fresh iron(III) hydroxide precipitate.¹⁴⁶

The solubility of the iron associated with the allophane appears to be less than that associated with kaolinite but only 24 hours were allowed for the interaction as against the 4 to 5 weeks found necessary to achieve true equilibrium.²⁷² The desorption of iron here is similar to that from a kaolinite surface, i.e., the cation adsorption site of the mineral, or from a polymeric hydroxide. The occurrence of this cation as its hydroxide in a separate phase would not be surprising as it has already been found for the more soluble aluminium and it was suggested in section 7.3.6 that a hydrolysable cation such as iron or aluminium would prefer to form a discrete phase, rather than be adsorbed by some other surface, at higher pH's such as those found in the soil.

Because it is much less mobile than aluminium iron(III) is unlikely to have a great influence on the chemistry of ion exchange sites associated with the aluminosilicate part of these clays.

8.3.3 Adsorption of Sodium by H-form Ohaupo Allophane

The adsorption of sodium from solutions of two different concentrations by H-form Ohaupo allophane (see section 8.2) is shown in figure 8.3. The adsorption characteristics displayed were similar to those usually seen for the adsorption of non-hydrolysed cations by hydrous oxides, i.e., a rapid rise in the uptake with increasing pH and the amount bound also increased with the concentration. However at higher concentration the adsorption isotherm

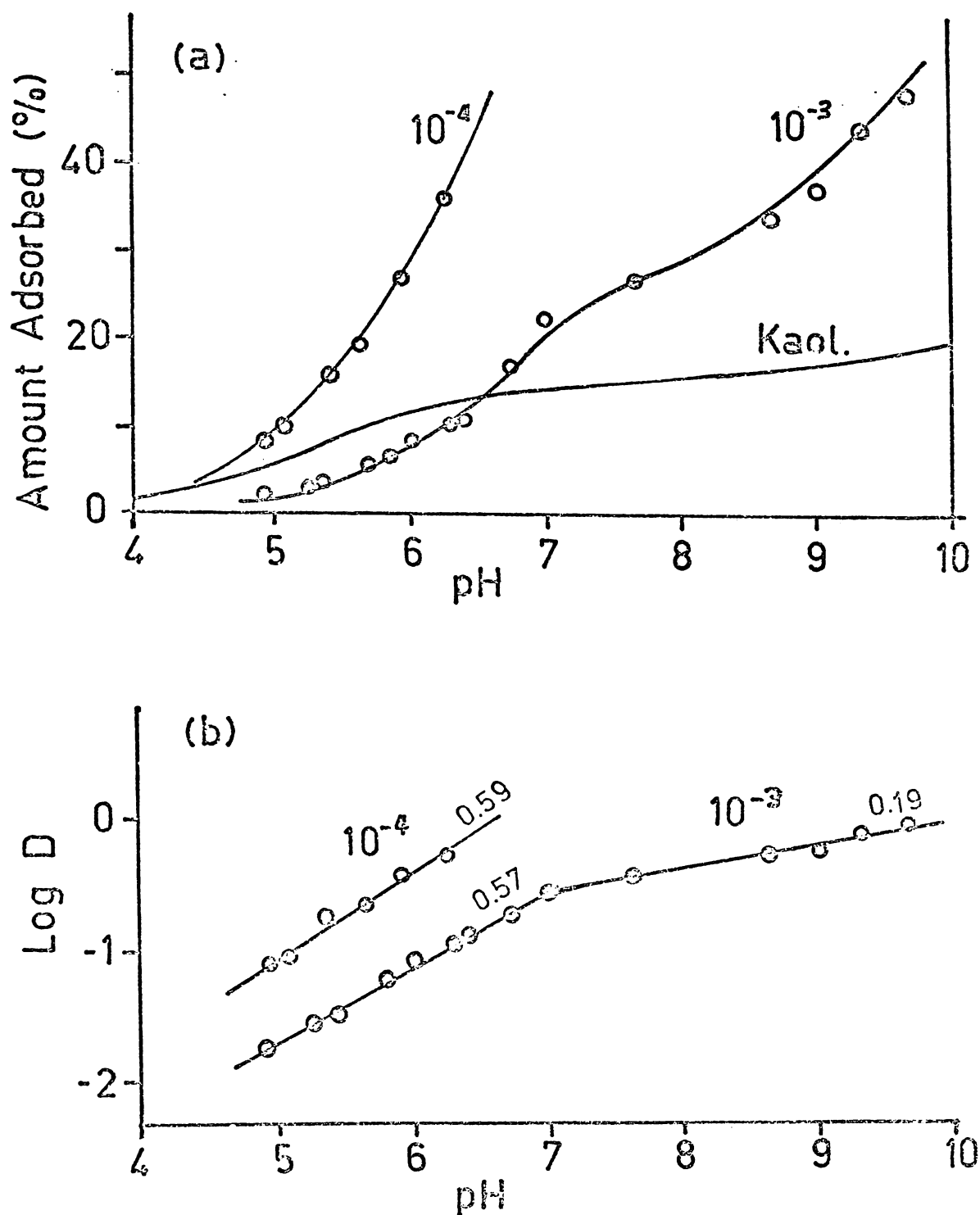


Figure 8.3. Adsorption of sodium by allophane and kaolinite. (a) Percentage adsorbed and amount adsorbed. (b) Logarithm of the distribution coefficient. Allophane concentration 3.5 g/l. (Kaolinite data taken from ref. 211. Comparison may be made between the curve for adsorption by kaolinite and the 10^{-3} M curve.)

appeared to have two parts with a transition at pH 7.

The hydrous oxide likeness is further confirmed by the variation of the logarithm of the distribution coefficient, $\log D$, with pH; this was linear (fig. 8.3b) and indicates that exchange for H^+ was a part of the adsorption process. (The numbers beside each line in the $\log D$ vs pH plots are the gradients determined by linear regression analysis.) The division of the isotherm into two parts is more obvious in this representation. That the lower pH parts are almost parallel is an indication that they may have been affected by the same mechanism; above pH 7 some influence appears to have been removed or added.

For low concentrations of adsorbate the proposed electrochemical model predicted a single value of $\log D$ (this model is summarised in section 7.3.8). That $\log D$ was not constant but decreased substantially with sodium concentration indicated a high occupation of adsorption sites. However the actual amount of sodium sorbed increased with concentration. Thus either the maximum amount of adsorption was concentration dependent or alternatively there was another competing cation present.

These suspensions of allophane contain both weak acid (aluminosilicate) cation adsorption sites and a form of aluminium hydroxide. It was predicted in section 7.3.6, and observed in section 8.3.1, that with acidification of such a mixture the hydroxide would gradually dissolve. Some of this released aluminium would readorb at the cation retention sites replacing the cations occupying them. The isotherms of the variation of the extent of adsorption of these secondary cations with pH would show a transition. This would be at the pH at which the aluminium concentration became sufficiently high for it to occupy a large proportion of the available sites. It is apparent that a process of this nature has occurred with allophane; below pH 7 sodium must compete for

adsorption sites with aluminium but not at higher pH's.

Similar competition from aluminium has been found for the adsorption of alkali metal cations, including sodium, by kaolinite.¹³⁵ On this clay there was observed to be a transfer of aluminium from the matrix to the cation adsorption sites. The transfer increased with acidification but the amount adsorbed decreased with sodium concentration, i.e., the sodium was able to compete successfully for adsorption sites.

The site-binding model suggests that in some situations the distance that an adsorbed cation apparently lies from the surface may be calculated. However there are two reasons why that may not be meaningful here. First, the surface appears to be close to saturation and most sites are occupied. Secondly, the determination of surface charge, by potentiometric titration, measured the adsorption of both H^+ and OH^- by all of the material, i.e., not only the aluminosilicate part but also the aluminium hydroxide fraction. Thus a value of $d\sigma_0/d\text{pH}$, needed to solve equation (7.97), would be a mean value for all surface components and not just the cation adsorption sites. Some quantitative discussion may still be made.

From (7.125) the difference between the slope of the $\log D$ vs. pH plot and the ion charge was shown to be a measure of the difference between the electrical potentials experienced by the two exchanging cations in the adsorbed state, or, from (7.90), the distance of the ion from the surface. Above pH 7 sodium may be competing with H^+ ; below this pH it competes with aluminium as well. As the slope was steeper when aluminium was the major competing species not only does sodium lie a distance from the surface but aluminium itself when adsorbed is also separated from the surface. It cannot be considered to become a part of the cation binding matrix in the same manner as H^+ . The order of apparent proximity to the surface was (closest first):

H^+ , $Al^{3+}/AlOH^{2+}$, Na^+ .

The adsorption of sodium by allophane also proceeded at a relatively low pH; even below pH 4.8, the PZC. By extrapolation of the log D vs. pH plots adsorption would still proceed below pH 3 even in the presence of competing aluminium.

The absolute quantity of sodium bound by this allophane may be compared with that reported to be adsorbed from a solution of similar strength by kaolinite.²¹¹ Although a 20-fold greater kaolinite concentration was employed this was matched by the greater surface area of allophane; the total surface area available in each case was 1100 m² per litre of suspension. Except at very low pH's the adsorption density on allophane was greater. The capacity of allophane to adsorb cations was influenced by pH to a larger extent than that of kaolinite.

8.3.4 Adsorption of Potassium and Sodium: Cation Selectivity

The adsorption experiments for all cations were carried out from dilute sodium chloride solutions. The results for the experimental determination of the adsorption of both potassium and sodium, from solutions of their chlorides by H-form Ohaupo allophane with varying pH, are shown in figures 8.4a and b. There are four points of note.

First, the adsorption of potassium was more favoured than that of sodium from a 10^{-4} M solution of its chloride (c.f. fig. 8.3a).

Secondly, the adsorption of sodium was little different from that in the absence of potassium, except that it was displaced to lower surface concentrations by an amount approximately equal to the amount of potassium adsorbed.

Thirdly, adsorption of potassium was influenced by pH to a lesser extent. From the slope of the log D vs. pH plot, which was lower for potassium than for sodium, potassium appeared to lie

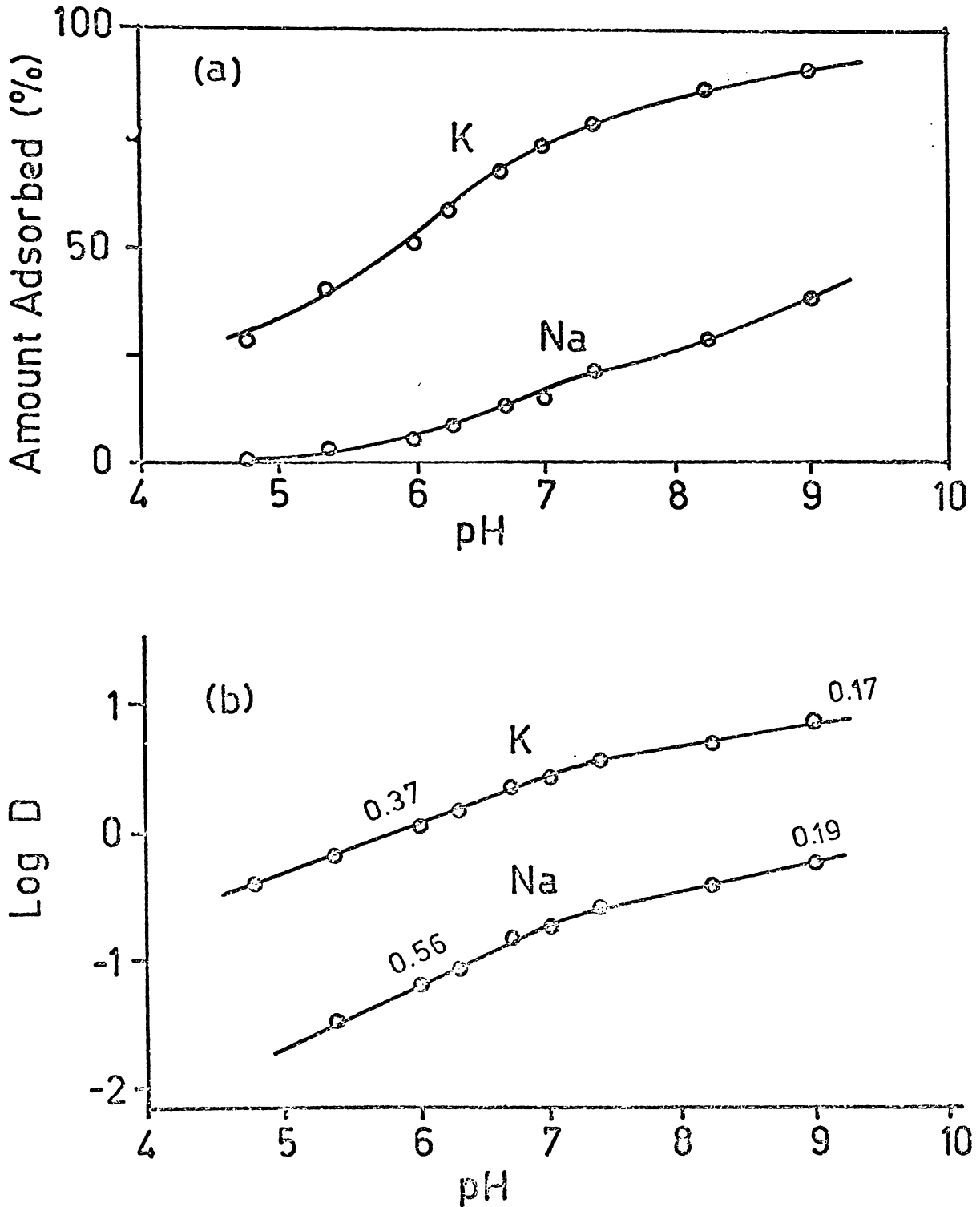


Figure 8.4. Adsorption of potassium and sodium from solution by allophane. (a) Percentage adsorbed. (b) Logarithm of the distribution coefficient. Clay concentration 3.5 g/l.

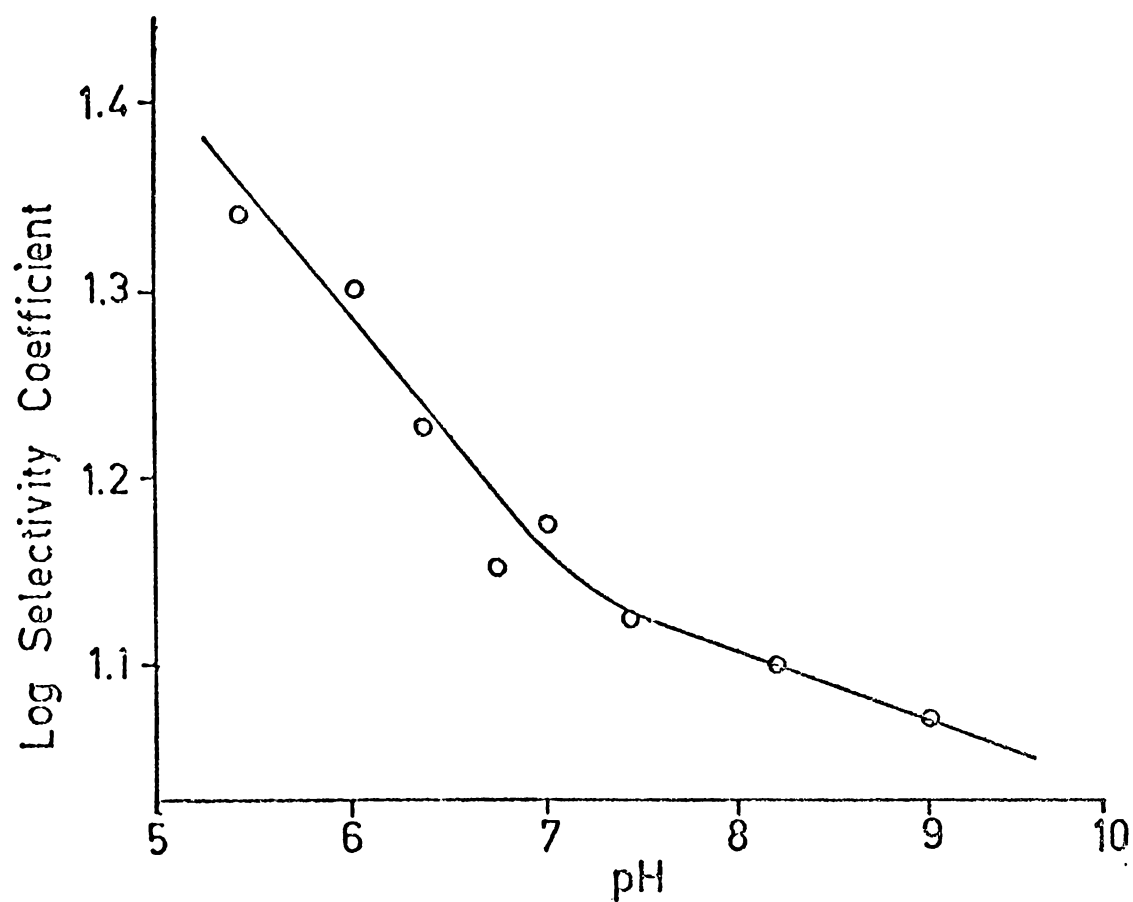


Figure 8.5. Variation of the logarithm of the coefficient of selectivity shown by allophane for potassium and sodium, i.e. K_{Na}^K .

further from the clay surface.

Fourthly, the change in the slope of the log D vs. pH plots, i.e., the competition from aluminium, occurred at the same pH.

As adsorption of the two cations was not totally independent the surface occupancy would have been high and approaching saturation. Thus at pH less than 7 both ions were competing with aluminium for adsorption sites; this third cation dominated the adsorption of the other two. As potassium is a more diffuse (low charge, large ionic radius) cation it was influenced to a smaller extent.

The differences between the abilities of the two alkali metal cations to adsorb at the allophane/aqueous interface are also reflected in their selectivity coefficients, K_{Na}^K , calculated from (7.102). The logarithm of this parameter should be linear with pH if the system here is described by the site-binding model. The variation of the coefficient of selectivity with pH is shown in figure 8.5. The relationship is approximately linear. This is in agreement with the prediction that as pH increases a hydrous oxide-like material would show an increasing relative preference for smaller cations although at the positive surface the selectivity would be in favour of more diffuse, low charge ions such as potassium (section 7.3.5).

Again allophane is showing its similarity to kaolinite. On this mineral the adsorption of sodium was found to be depressed by competition from aluminium to a greater extent than the adsorption of either potassium or caesium.¹³⁵

8.3.5 Adsorption of Strontium: Influence of Electrolyte Concentration

The adsorption of strontium by H-form Ohaupo allophane produced sigmoid-shaped curves of uptake against pH (fig. 8.6a), similar to those which are characteristic for hydrous oxides. For the most

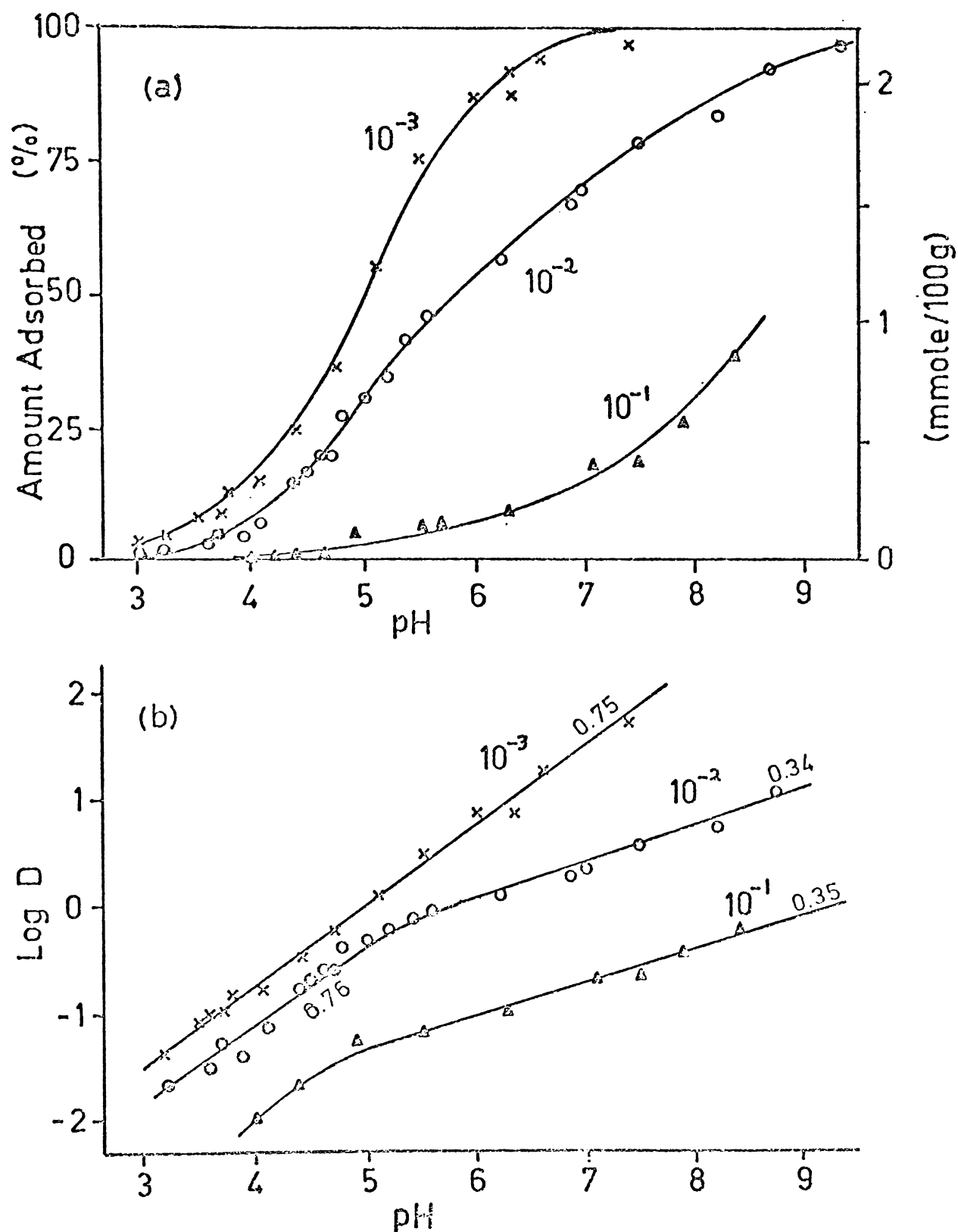


Figure 8.6. Variation of the adsorption of strontium by allophane with pH and electrolyte concentration. (Numbers on plots refer to sodium chloride concentration or slope of the plot determined by least squares analysis.)

dilute sample a large change was found in the relatively short pH range of 3 to 5. This was below both the PZC (4.8) and the IEP (6.3) of this clay, and it is the only major difference immediately obvious between the adsorption by allophane and the common hydrous oxides (e.g., refs. 130, 171 or 180). High adsorption of this nature below the PZC has usually been indicative of a high dielectric constant.^{102,197} (This is the cause of the high adsorption below the PZC displayed by rutile,²⁷³ the only other material to display this behaviour.) However, allophane, like the other aluminosilicates, is likely to have a low dielectric constant.⁵¹ The high adsorption at low pH must have some other origin.

The surface charge of allophane is the combination of the effects of weakly basic aluminium hydroxide and weakly acidic aluminosilicate surface group ionisations. As the surface components exist as discrete units, at the PZC there will be extensive development of both negative and positive charge sites. The high adsorption of the cations is in response to this negative charge.

The log D/pH plots for the adsorption discussed above (fig. 8.6b) were all linear; exchange for H^+ was again involved in the adsorption process. The adsorption of strontium was more pH dependent than that of the monovalent cations, potassium and sodium. From the model this would be caused by its higher charge; each adsorbing strontium ion releasing two H^+ . The isotherms for the lower concentration systems, being steeper, would represent the adsorption of the cation in competition with aluminium whilst at higher concentration (10^{-3} M) the aluminium has been displaced by strontium; at least at pH greater than 5. As 10^{-3} M sodium was capable of excluding the aluminium from retention sites only above pH 7 it can be seen that strontium is much more effective in this respect.

Increasing the concentration of the background electrolyte had

only a small effect on strontium uptake below pH 5 for 10^{-2} and 10^{-3} M sodium chloride solutions but above this pH and these concentrations the changes were quite significant and resulted in much less strontium being adsorbed (fig. 8.7a and b). Only two slopes were evident in the log D/pH plots; viz., 0.35, when the adsorption was only in competition with sodium, and 0.75, when aluminium adsorption was also occurring. The extension of the region of reduced slope to lower pH by increasing sodium chloride concentration would be the result of the ability of sodium to displace aluminium from the surface. To do this very high concentrations were needed. At the same time that sodium was able to displace aluminium it was of course capable of displacing strontium. In concentrated sodium chloride solutions the adsorption of strontium was in this way greatly reduced.

8.3.6 Adsorption of Strontium: Concentration Effects and Apparent Surface Saturation

In figure 8.7 an increase in the concentration of strontium increased the quantity adsorbed. A number of experiments were carried out to determine the adsorption of strontium from solutions of increasing strength onto H-form Ohaupo allophane. A typical result is shown in figure 8.8. The available surface appeared to become saturated from dilute solution, as low as 10^{-3} M in this case. With an increase in the pH both the minimum concentration required for saturation and the amount of cation adsorbed increased.

The maximum cation adsorption densities determined from the constant pH adsorption isotherms, using the Langmuir equation (6.5), are shown in figure 8.9a. The proportion of the total surface area (BET N_2) that would be covered by fully hydrated cations is ^{N₂} also shown. The maximum adsorption density appeared to increase exponentially with pH (this was confirmed by the linearity of the logarithmic plot,

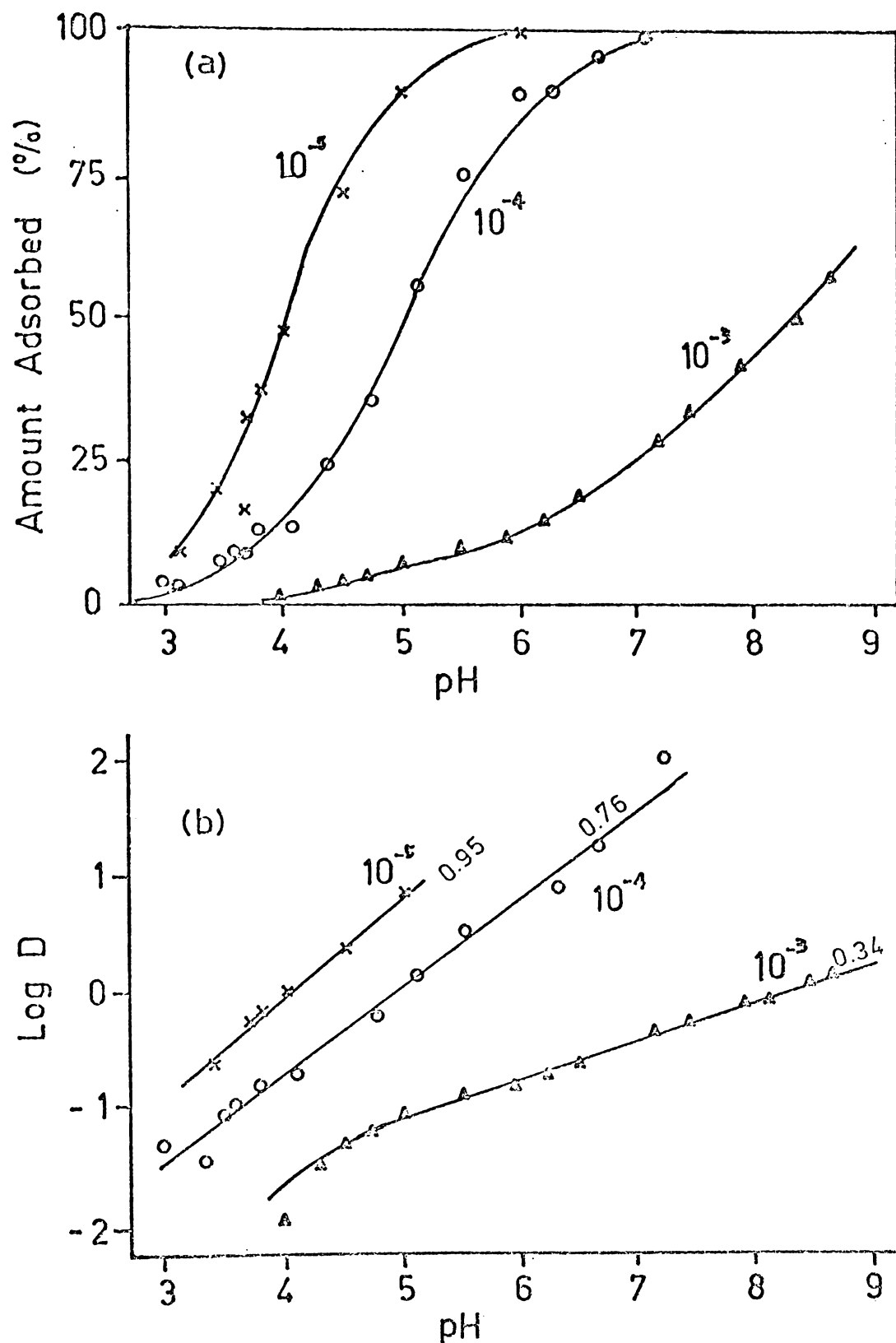


Figure 8.7. Variation of the adsorption of strontium by allophane with pH and strontium concentration. H-form Ohaupo clay, concentration 3.5 g/l.

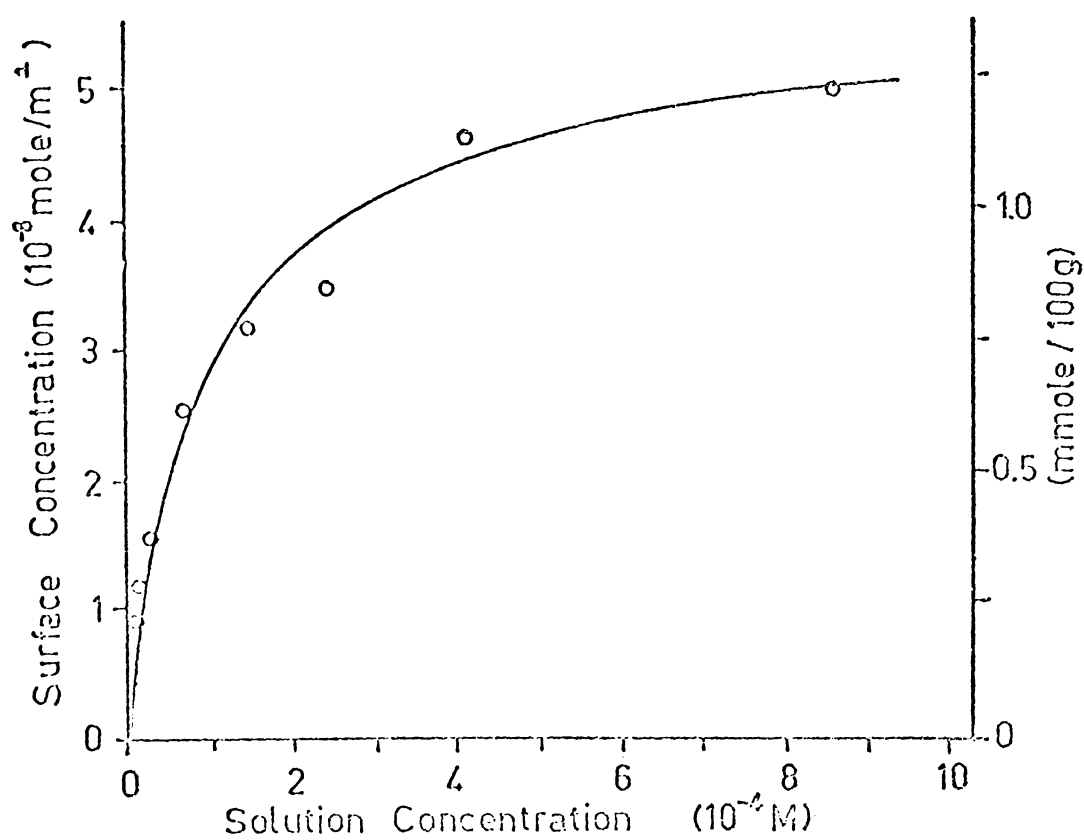


Figure 8.8. Variation of the adsorption of strontium by allophane at constant pH (5.0) as a function of strontium concentration. Allophane concentration 3.5 g/l.

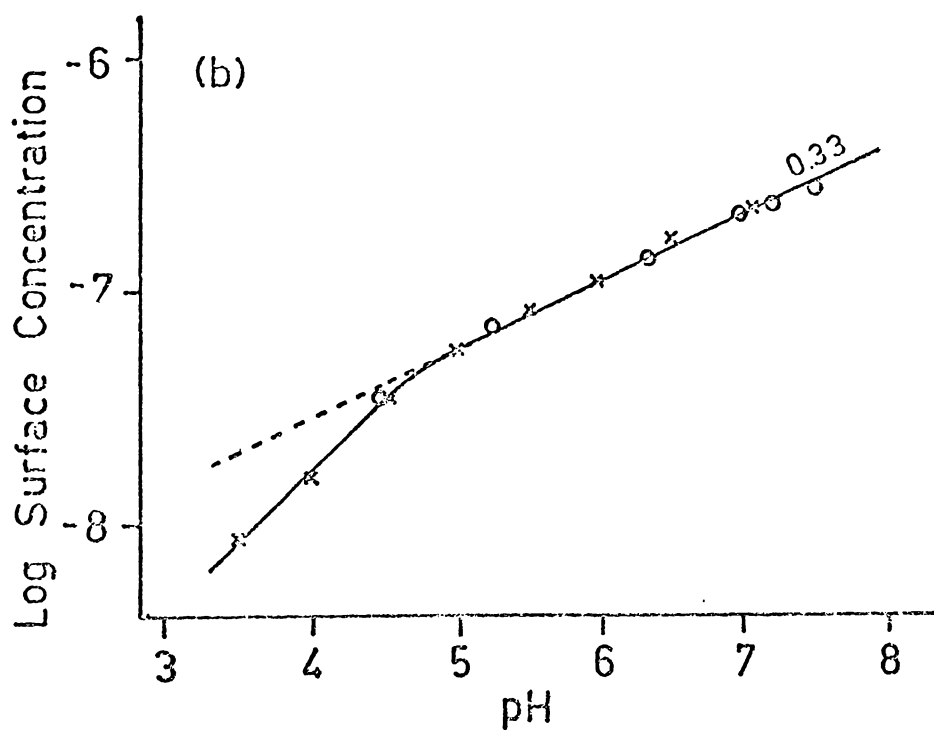
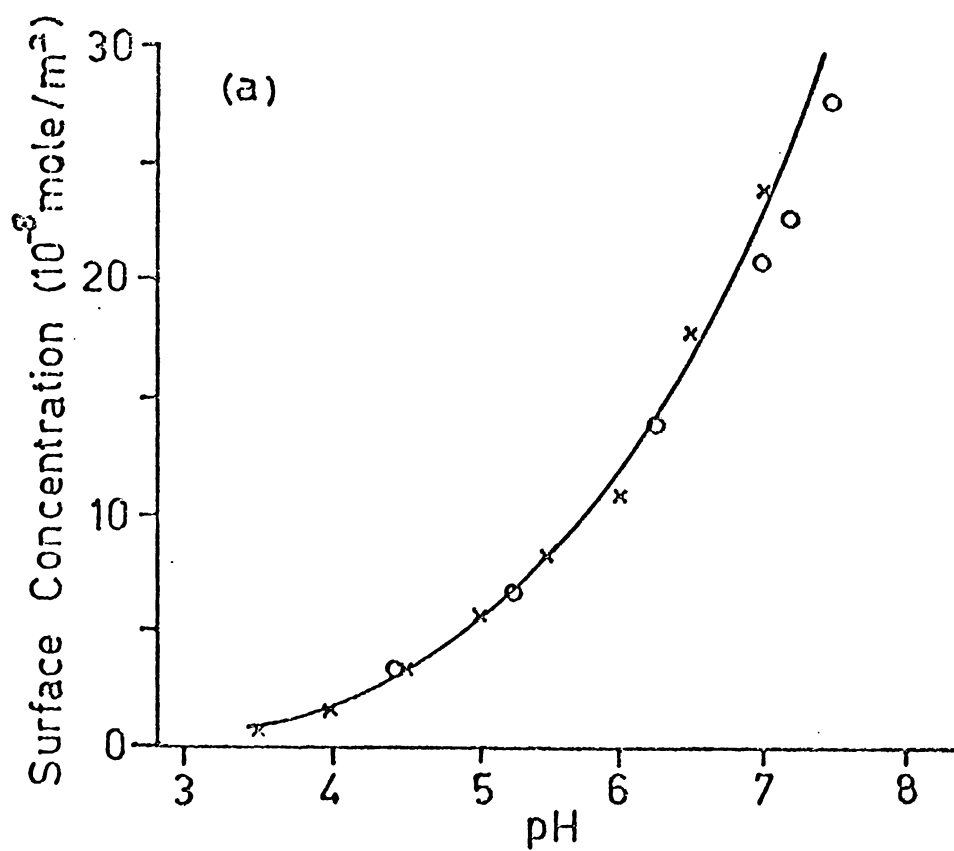


Figure 8.9. Variation of the maximum adsorption capacity of allophane for strontium with pH. (a) Maximum surface concentration, (b) logarithm of the maximum adsorption capacity.

fig. 8.9b) in a manner similar to the increase reported for cation adsorption by the hydrous oxides goethite¹¹⁰ and alumina,¹⁷⁹ or anion adsorption by allophanic soils.¹⁵⁸ The slope of the logarithmic plot is almost the same as that for alumina, figure 6.1b, i.e., 0.33 vs. 0.36. Included in both parts of figure 8.9 are the values of the cation surface densities at which changes in the slopes of the log D/pH plots were recorded. There is a high correlation between these points and the maximum cation adsorption density. It appears that the total number of sites for the adsorption of cations by allophane was effectively exponentially dependent upon the pH, i.e., it was inversely related to $[H^+]$.

As the strontium concentration was relatively high, only at low pH was aluminium competition evident. This induced the apparent maximum surface concentration below pH 4.5.

The rate at which the logarithm of the maximum strontium surface concentration increased with pH equalled $d \log D/d \text{ pH}$ for strontium adsorption in the absence of competition from aluminium adsorption, viz., 0.35. It is likely that the same correlation exists for the maximum surface concentrations for the other cations. Thus for sodium and potassium this property of the surface would increase at a lower rate than for strontium. Consequently the surface charge determined in the presence of strontium would increase more rapidly with pH than when measured in the presence of sodium alone.

8.3.7 Adsorption of Different Cations

The pH dependence of the adsorption of a number of cations from dilute solution by the various forms of Ohaupo allophane are shown in figures 8.10, 8.11 and 8.12. The overall preference order at pH 6.0 was: $Pb^{2+} \gg Sr^{2+} \sim Co^{2+} > Ca^{2+} > Tl^+ > K^+ > Na^+$. The selection was for ions with high charge and large radius, i.e., it followed the

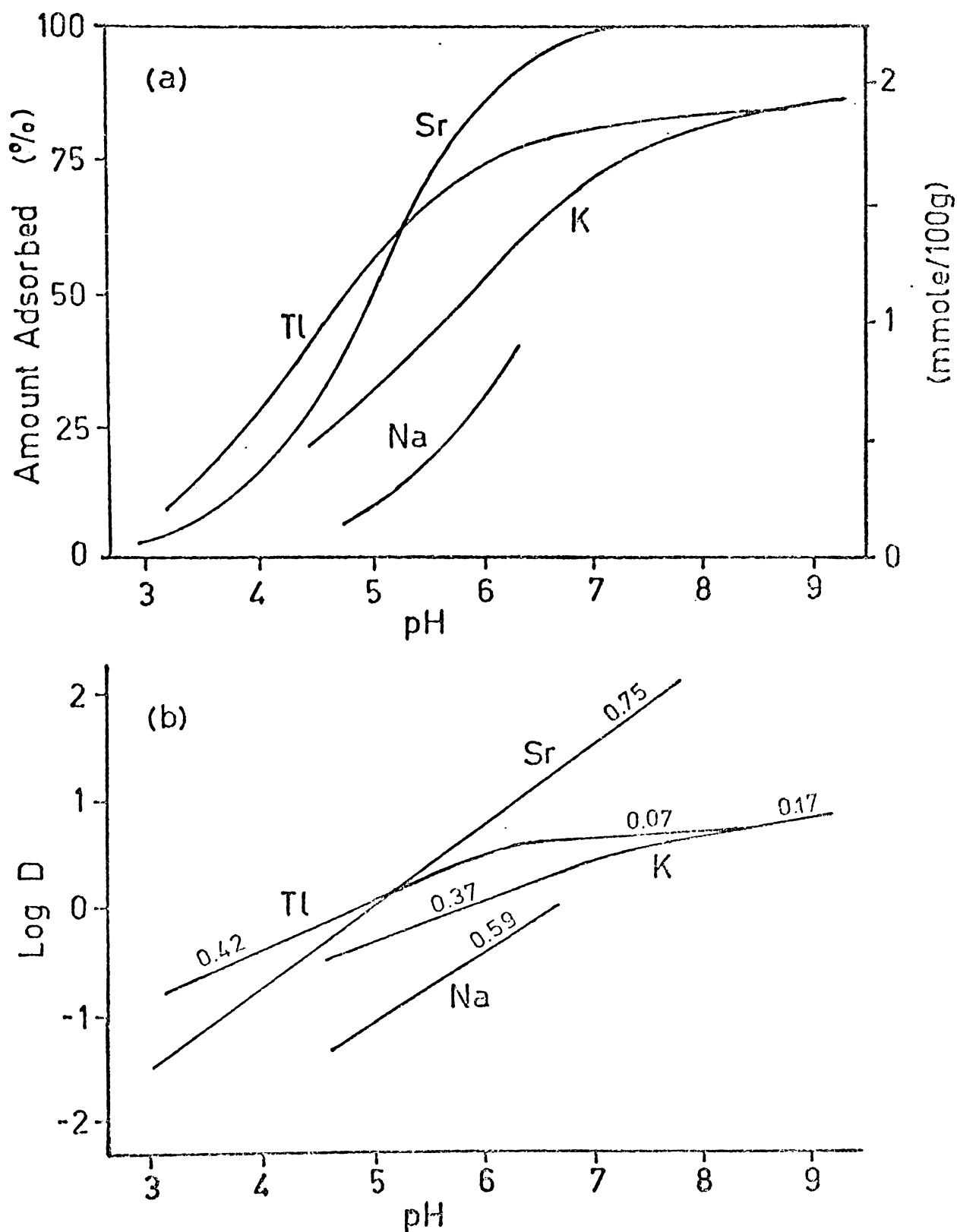


Figure 8.10. Variation of the adsorption of several different cations from 10^{-4} M solutions in 10^{-3} M sodium chloride (except for sodium which is from 10^{-4} M solution) with pH by H-form (mild-acid treated) Ohaupo allophane.

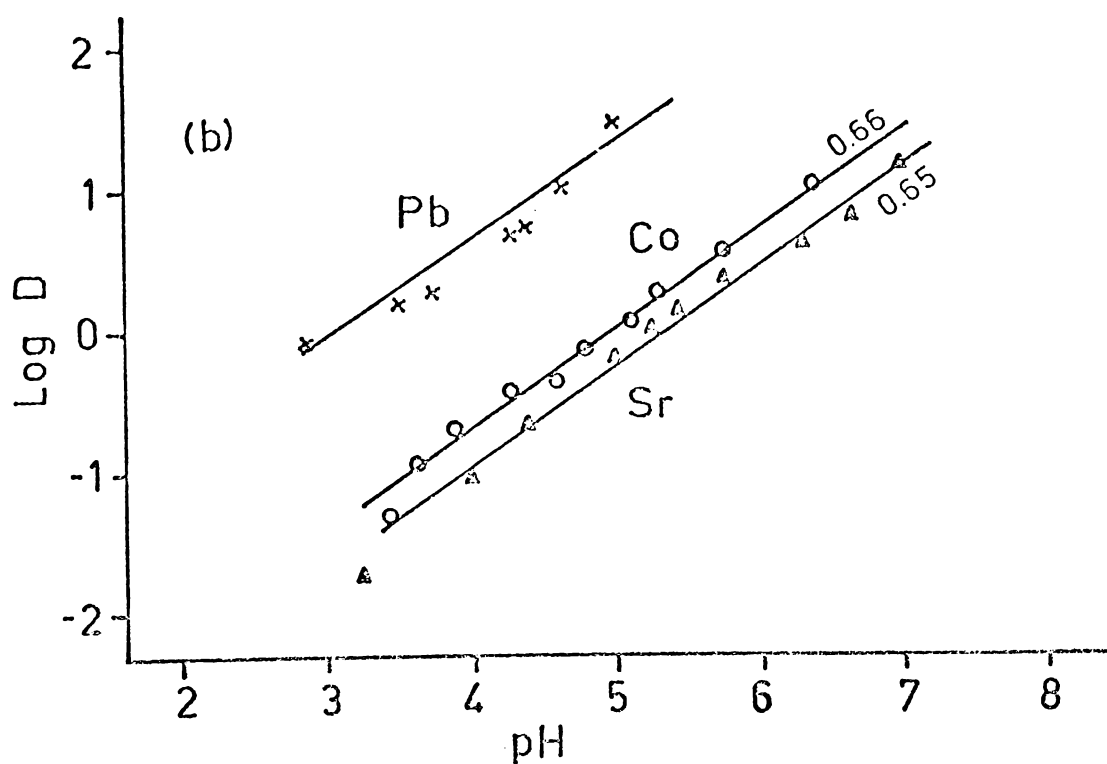
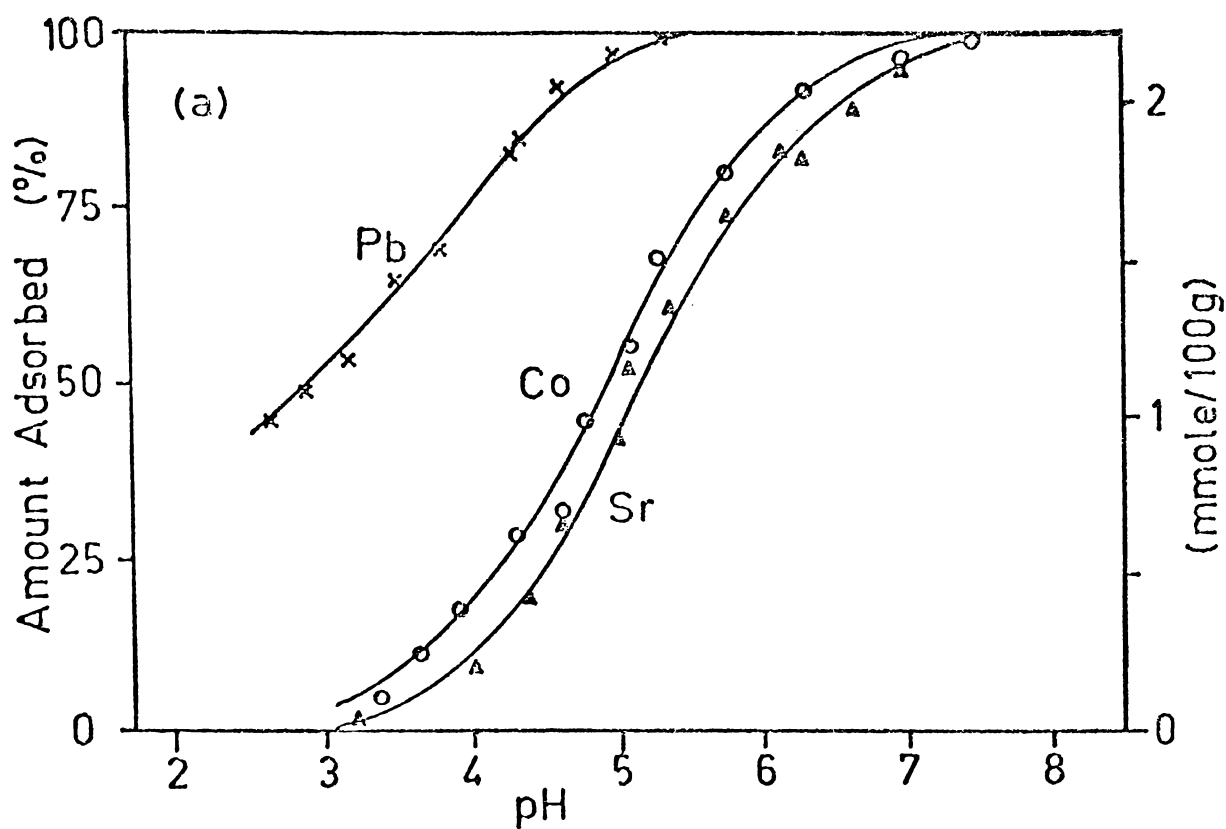


Figure 8.11. Variation of the adsorption of several different cations from 10^{-4} M solution in 10^{-3} M sodium chloride with pH by sodium-form Ohaupo allophane.

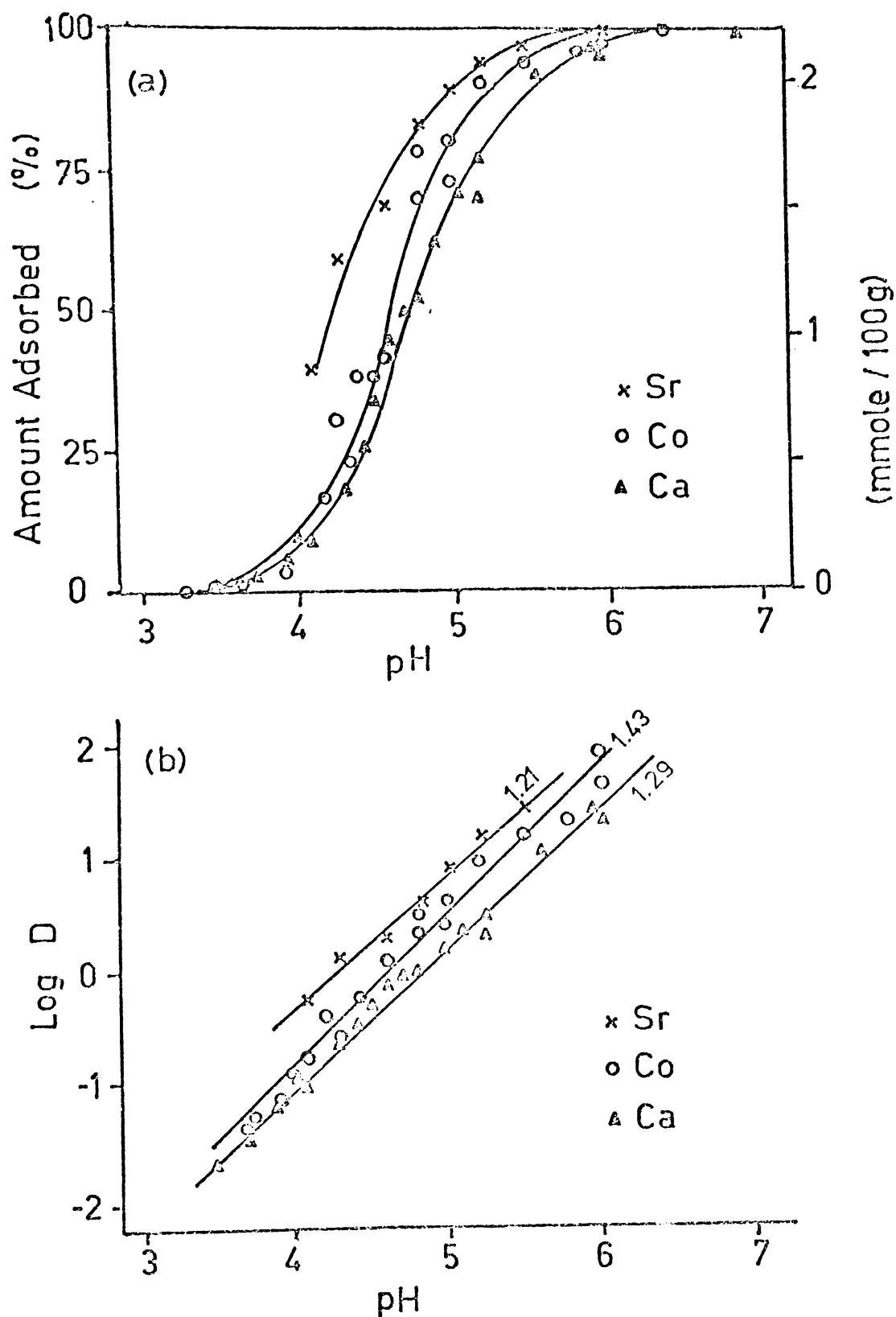


Figure 8.12. Variation of the adsorption of several different cations from 10^{-4} M solutions in 10^{-3} M sodium chloride with pH by acid-form Ohaupo allophane. Clay concentration 3.5 g/l.

lyotropic series and is similar to that found for the CEC by other workers.^{164,241,242} At pH 4.0 the preference order was: $\text{Pb}^{2+} \gg \text{Tl}^{+} > \text{Sr}^{2+} \sim \text{Co}^{2+} \sim \text{K}^{+} > \text{Ca}^{2+} > \text{Na}^{+}$. The selection for large ion size was much stronger at this lower pH.

Again the log D/pH plots were linear but the slopes for the divalent cation distribution were steeper than for the monovalent cation distribution and so they tended to intercept at low pH. The diffuse, low charge cations such as Tl^{+} and K^{+} were actually adsorbed more strongly from acid solution than any of the divalent cations except lead. The distinctly different position of lead may be the result of its readiness to be hydrolysed even in weakly acid solution; it is the only cation studied here that would be significantly hydrolysed.¹⁴⁶

From the differences between the gradients of the log D/pH plots and the ion charge, the similarity of the ion to the cation with which it is exchanging can be estimated, i.e., from the term $1 - (d \log D / dz \text{ pH})$. Below pH 6 the adsorption was in competition with, or exchange for, aluminium. The order of similarities at this pH was: $\text{Na}^{+} > \text{Ca}^{2+} > \text{K}^{+} \sim \text{Tl}^{+} \sim \text{Sr}^{2+}$, i.e., the reverse of the preference order at pH 5, the PZC.

The two effects found here are the reverse of those found for goethite¹⁸⁹ (see section 7.3.4). Here it is the small ionic cations that show the most similarity to the replaced cation. Below pH 6 this means similarity to Al^{3+} (small, highly charged) and ionic nature are determining the pH dependence and not (except perhaps for lead) the ability to form covalent bonds with the surface. Thus large ionic radius and low charge (where the surface is positively charged) encouraged retention; the adsorption of the non-hydrolysed cations was an ionic process, not a covalent process.

Above pH 6 for cation adsorption by H-form clay from the various

figures, the slopes of interest still showed the same order of similarity to displaced cation, i.e., $\text{Na}^+ > \text{Sr}^{2+} \sim \text{K}^+ > \text{Tl}^+$. In this region, although the surface appeared saturated, the adsorption was proceeding by exchange for H^+ . The small and the highly charged cations had the greatest pH dependence, the most likeness to H^+ . That the slopes were so low would indicate that the adsorbed cation was not closely associated with surface, but some distance from it. Thallium adsorption in particular was almost independent of pH; a result of its large ionic radius (at 0.144 nm¹⁸³ it was the largest cation studied here). Like caesium,¹³⁵ thallium can compete most successfully with aluminium. Consequently it occupied a unique position here in that it was more strongly adsorbed, at low pH, than any non-hydrolysed divalent cation.

8.3.8 Influence of Treatment of Allophane with Acid on Cation Adsorption

Mild acid washing (i.e., at pH 3 with dilute hydrochloric acid) of the sodium-form Ohaupo clay increased its tendency to adsorb cations from aqueous solutions (figs. 8.10, 8.11 and 8.13). It also increased the slope of the log D/pH plot, for strontium adsorbing in competition with aluminium, from 0.66 to 0.75. The effect of this treatment was to remove readily exchangeable cations, such as sodium and calcium as well as a small amount of aluminium. It would be expected to make more adsorption sites available and remove cations competing for them.

A much greater adsorption capacity was realised by strong acid washing using 0.1 M hydrochloric acid. For equivalent solutions, the isotherms for divalent cation adsorption by acid-form Ohaupo allophane were a full pH unit lower than those discussed above (fig. 8.13). The treatment given this clay was also sufficient to reduce its IEP to less than 4, as determined by flocculation (see Chapter Ten).

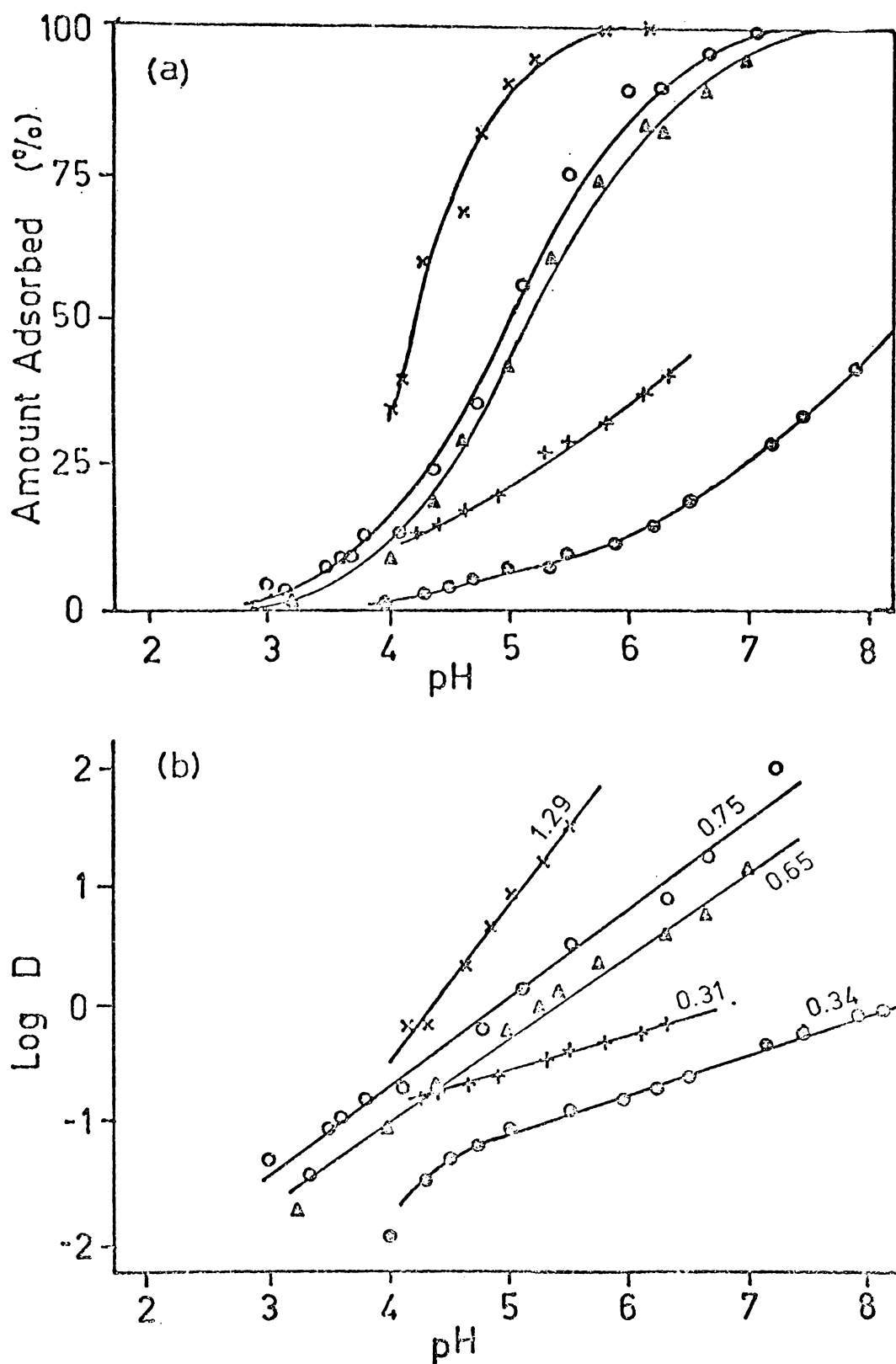


Figure 8.13. Variation of the adsorption of strontium by various forms of Ohaupo allophane with pH and concentration. $\times$ 10^{-4} M, acid form; $+$ 10^{-3} M, acid-form; $\circ$ 10^{-4} M, H-form; $\bullet$ 10^{-3} M, H-form; $\blacktriangle$ 10^{-4} M, sodium-form.

The increase in the cation adsorption capacity is consistent with the loss of a positive charge component, in this case octahedral aluminium, which occupied some adsorption sites. This would make the surface more negatively charged (hence the low IEP) and lower the amount of aluminium available to compete with the adsorption of other cations. Thus acid washing of allophane reduced its amphoteric nature and reinforced its weak acid character.

8.3.9 Adsorption of Strontium by some Waikato Clays

The adsorption of strontium, from a 10^{-4} M solution in 10^{-3} M sodium chloride, by the sodium forms of each of the three clays used in this study is shown in figures 8.14a and b. The adsorption onto the Tirau allophane was the most strongly influenced by pH but it also had the greatest capacity commensurate with its large surface area. Except that it had a lower capacity Mangawara halloysite displayed very similar adsorption characteristics to those of the Ohaupo allophane. The change in the slope at pH 5.8 in the log D/pH plot for this clay corresponded to a surface density of strontium ions of only 8.5×10^{-8} moles m^{-2} , i.e., 80% of the occupancy of saturation of the Ohaupo allophane surface at the same pH. The slopes of the log D/pH plots were both similar at high pH.

The differences between the Tirau and Ohaupo allophanes suggests that the surface of the former was influenced to a greater extent by pH in the region of interest. It was seen in section 8.3.1 that the equilibrium concentration of aluminium in the suspension of the Tirau allophane was much more pH dependent than that for the Ohaupo clay. Thus the influence of this cation upon the adsorption of other cations will be more pH dependent.

The similarity between the Ohaupo allophane and the Mangawara halloysite is noteworthy as it implies that the cation adsorption

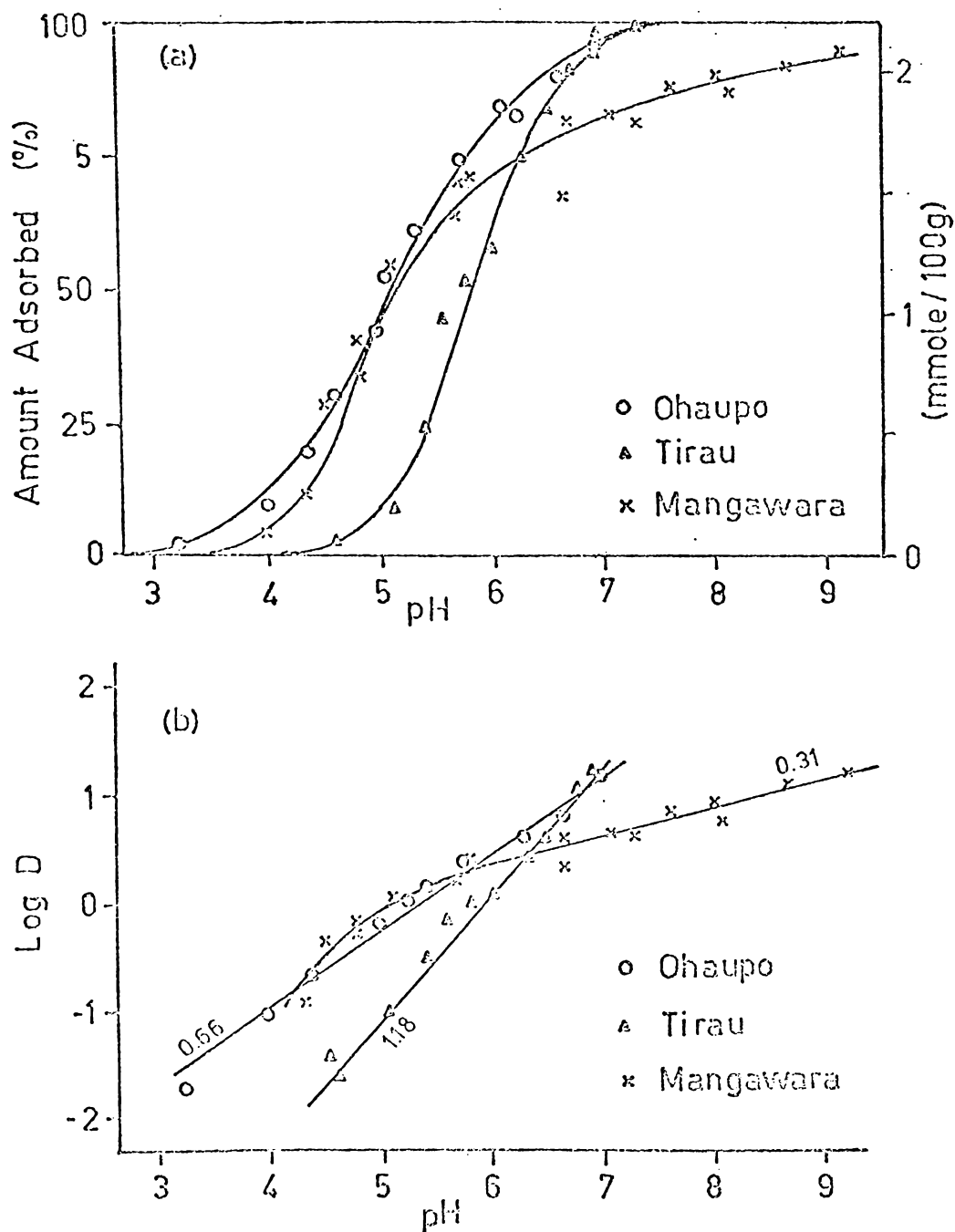


Figure 8.14. Variation of the adsorption of strontium by several different clays with pH. Clay concentration 3.5 g/l. Strontium concentration 10^{-4} M, in 10^{-3} M sodium chloride.

sites of these two materials are alike. The halloysite surface does not differ greatly from that of the mineral kaolinite so that in this respect kaolinite, halloysite and allophane may have similar cation adsorption sites. These are associated with the aluminosilicate matrix and in each case they are modified differently by the proximity of hydrolysed aluminium.

8.4 Summary of the Interactions of Allophane with Cations

The nature of allophane was investigated by studying the interactions with dilute solutions of cations at various pH. The influence of acid treatment of the clay upon these interactions was also studied. The following properties were discovered and a number of conclusions were reached.

Allophane contains aluminium in a form similar to polymeric hydrous aluminium oxide. This aluminium is acid soluble and from acid solutions it can adsorb onto cation adsorption sites associated with the aluminosilicate part of the mineral. In doing so it displaces other cations. If the pH is increased the aluminium leaves the cation retention sites and returns to the hydrous oxide phase; its place at the adsorption site being taken by another cation. In a similar way iron(III) may also be present as a discrete hydrous oxide.

The adsorption of sodium by allophane was found to be significant below the PZC of the clay and it increased with pH. Below the PZC the adsorption was the result of the development of separate regions of positive and negative charge, and not, as with hydrous oxides, caused by a high dielectric constant. Exchange for H^+ from surface hydroxyl groups was involved in the adsorption.

Below pH 7 sodium adsorption, from 10^{-3} M solution, was in competition with aluminium adsorption; with an increase in the sodium concentration in solution aluminium was displaced from the cation

retention sites. In the absence of other cations the sites were occupied by aluminium. In all cases the surface acted as though it was saturated or approaching saturation.

Cation selectivity was found to be related to ion charge, ionic radius, ease of hydrolysis and pH. Cations, such as lead(II), that hydrolyse readily were adsorbed most strongly. At low pH large, low charge cations were the most strongly adsorbed; e.g., Tl^+ and K^+ . These were also the least effected by pH change and by the presence of competing aluminium. At higher pH smaller highly charged cations became more favoured; e.g., Ca^{2+} and Co^{2+} . The preference order at pH 4.0 was: $\text{Pb}^{2+} \gg \text{Tl}^+ > \text{Sr}^{2+} \sim \text{Co}^{2+} \sim \text{K}^+ > \text{Ca}^{2+} > \text{Na}^+$ but at pH 6.0 it was: $\text{Pb}^{2+} \gg \text{Sr}^{2+} \sim \text{Co}^{2+} > \text{Ca}^{2+} > \text{Tl}^+ > \text{K}^+ > \text{Na}^+$.

Thallium occupied a unique position by being more strongly adsorbed, at and below pH 4.0, than any non-hydrolysed divalent species.

The apparent maximum surface concentration of adsorbed strontium was found to increase exponentially with pH. Below saturation the amount adsorbed at constant pH increased with solution concentration. This cation could also be displaced, and prevented from adsorbing, by both aluminium and high concentrations of sodium. The maximum surface concentrations for other cations also appeared to increase exponentially with pH but with different exponents. For sodium and potassium these were much less than that for strontium; for thallium the maximum surface concentration appeared to be almost pH independent.

For constant concentrations of all the non-hydrolysing ions the variation of the distribution of the cation between the solution and the adsorbed state could be described by two linear equations of the following form;

(i) at low pH (adsorption in competition with aluminium)

$$\log D = a + b\text{pH},$$

(ii) at higher pH (adsorption with no competition from aluminium)

$$\log D = a' + b'pH,$$

a and a' were functions of the nature and concentrations of the cation and also of all competing cations. b and b' were functions of the nature of the adsorbing cation. The point of intersection of the two linear parts was dependent upon the concentration of all adsorbing species. The constant b' also related the logarithm of the maximum surface concentration to the pH.

Acid washing of allophane increased its capacity to bind cations; this process removed aluminium and some iron(III), probably exposing cation adsorption sites on the aluminosilicate core associated with the mineral's permanent negative charge. After acid treatment these sites were initially occupied by H^+ but, as with other clay minerals, this was slowly replaced by aluminium.

Allophane displayed a number of similarities to cation adsorption by hydrous oxides. These included increased adsorption with pH, similar selectivity near neutrality, a pH dependent maximum adsorption capacity, and the adsorption process was an exchange for H^+ . A number of differences were also obvious. These included the influence of the aluminium present (which introduced interference at low pH), a lower dependence upon pH, and, as a result of the permanent negative charge, greater adsorption below the PZC.

The ways that allophane differed from the hydrous oxides were related to the properties it has in common with kaolinite. These are the cation adsorption site being associated with the aluminosilicate, and the influence of the aluminium. The pH dependence of the cation interactions displayed by allophane was also greater than for kaolinite. Allophane was found to have a larger capacity to adsorb cations than kaolinite and halloysite except at low pH; the capacity was still less than that of montmorillonite.

In its cation interactions allophane occupies a position between the hydrous oxides and the aluminosilicate clay minerals. This would be because allophane is an aluminosilicate onto which a hydrous oxide has been deposited.

Cation adsorption by allophane displayed many features that were predicted by the proposed model for ion adsorption at the hydrous oxide/aqueous interface (this model was summarised in section 7.3.8). However, without a full solution of the model the complete applicability cannot be determined. It is possible that because of the variable nature of the allophane surface extra factors would need to be introduced. Nevertheless, the proposed model provides a basis for the mathematical interpretation of the behaviour of allophane in aqueous electrolyte.

8.5 Conclusion

The nature of the cation adsorption site of allophane and the form of the hydrolysed aluminium associated with the surface of this mineral have been determined. This aluminium was found to have a strong influence upon the adsorption of other cations by allophane.

The cation characteristics that influence their adsorption by allophane have also been determined. These are the properties that have been found to influence cation adsorption by the hydrous oxides. They are also the properties found to be important in the electrochemical consideration of the adsorption discussed in Chapter Seven.

The electrochemical theory proposed in Chapter Seven assisted explanation of the observed cation adsorption phenomena. In particular, a simple linear relationship was found between pH and the logarithm of the distribution coefficient of the cation, a parameter which described the partitioning of the cation between the surface and the solution.

8.6 Possible Applications in Industry

Allophane has the capability to bind firmly multivalent anions, such as phosphate and arsenate, and hydrolysed cations such as iron(III), lead and aluminium. Other cations that do not hydrolyse can also be efficiently removed from dilute solutions. The presence of other cations and acidification both reduce the efficiency, sometimes markedly. These ion interaction properties mean that allophane is very active in the soil where it may control the availability of many nutrients, particularly phosphate and molybdate.^{158-161,257} The firm binding of the nutrient cations, such as cobalt and potassium, which is reversible, gives allophane domination over soil fertility. The binding of the anions like phosphate would indicate that natural water systems which contain suspended allophane may become depleted in available major nutrients. This may provide a method of transport of nutrients out of solution and growth cycles to sediments. As allophane has a high aluminium hydroxide content to which adsorbed anions may be associated even anaerobic conditions, which solubilise iron-bound phosphate, would have little influence on allophane-bound phosphate.

The addition of allophane to effluents would bring about a reduction in the concentration of soluble ionic components such as phosphate. Recovery of the allophane in a sludge would provide a source of the bound material as phosphate is not totally irreversibly held by this clay although it may be released only slowly.

The use of allophanic tephra (the whole part of the soil) for further purification of treated sewage effluent has been investigated with some success and significant reductions in the inorganic phosphate content were achieved.²⁷⁴ A proposed method of treating the effluent involved passing it through columns of loosely packed tephra.

The ability to adsorb heavy metals such as lead and thallium effectively would allow allophane to be used for treatment of effluents containing such species. These include those from geothermal power installations, nuclear fuel processing operations and electroplating plants. Effluents from the last two types of industry may contain anions not desired in the natural environment. After contact of these, either with suspended allophane or with allophanic soil, it would be anticipated that their toxicities may be substantially reduced by adsorption of the ions.

CHAPTER NINE

ELECTROPHORETIC STUDIES AND THE ISOELECTRIC POINT

9.1 Introduction

The nett electric charge of a colloidal particle controls, to a large extent, its interaction with other colloids. This same charge also determines the colloids' behaviour in electric fields generated by external sources, an effect used in electrophoresis. Because this allows the charges to be studied, electrophoresis has become invaluable in studies of the surface and colloid chemistry of hydrosols.

A reliable electrophoretic apparatus became available only when this study was near completion and so its use was limited to the few experiments described. In particular, the alteration of the surface properties of allophane by the dithionite-citrate reagent (a reagent commonly used for the removal of hydrous iron(III) oxides from clays and soils) was investigated by this means.

9.2 Electrophoresis and the Zeta Potential

The four previous chapters have discussed chemical processes that occur at, or close to, the clay mineral or hydrous oxide surface. These processes can result in such colloids becoming electrically charged; if they are subjected to an electric field they will tend to migrate towards the electrode bearing the opposite charge. This phenomenon, the migration of charged particles through a liquid as the result of the imposition of an external electric field, is known as electrophoresis. From determinations of the particle velocity of ideal suspensions information about the potential difference between the plane of shear between the phases and the bulk liquid can be obtained. This potential difference is known as the electrokinetic or zeta potential, ζ .

The problem of interface definition again arises. It is essential to decide where the plane of shear is in the double layer, i.e., which part of the double layer can be considered to be a part of the solid and which a part of the liquid. In general, at the solid/aqueous interface the solid binds one or more layers of water molecules strongly and this forms a fixed or stationary layer which will travel with the particle. For simplicity it is usual to consider that the division between the fixed layer and the solution (i.e., the shear plane) is discrete. (This implies a discontinuity in the viscosity rather than the continuous variation expected because of the thermal mobility such layers experience.) Provided at least a part of the diffuse layer is outside the shear plane ζ will be influenced by all phenomena that effect the potential at the inner boundary to the diffuse layer (the outer Helmholtz plane or OHP), i.e., ψ_d (see fig. 4.2). That is if ζ is a diffuse layer potential it will be described by the equation (4.38) with x being the distance from the surface to the shear plane.

Thus ζ will:

- (i) be reduced in magnitude by an increase in the total ionic strength,
- (ii) become more negative with an increase in the concentration of anions that are potentially determining or strongly adsorbed in the Stern layer, and
- (iii) become more positive with an increase in the concentration of cations that are potential determining or strongly adsorbed in the Stern layer.

These influences have been found with hydrosols and so the shear plane will lie outside the OHP. Correlation of experiment and double layer theoretical predictions have not been sensitive to the positioning of the shear plane at or beyond the OHP¹⁵⁴ and so it is commonly assumed that $\psi_d = \zeta$.

Electrophoresis is useful for observing nett ionic interactions within the fixed layer at the solid/solution interface. As the electrical charges that affect electrophoretic mobility are those that are involved in the stability of colloidal dispersions (see Chapter Ten), electrophoresis is commonly used to predict the conditions under which flocculation may proceed. Generally for a dispersion of a single material flocculation is most rapid at its isoelectric point (IEP). At this point the particle has no nett charge, $\psi_d = \zeta = 0$, and the particle will not be induced to move by the application of an electric field. This point can be readily determined by electrophoresis.

The physical property measured by electrophoresis is the electrophoretic mobility, em , given by v_e/E where v_e is the velocity induced in the particle by an electric field of intensity E . If the body is positively charged it will obviously migrate towards the cathode whilst when it bears a negative charge it will approach the

anode; this sign must be incorporated in the particle velocity.

Electrokinetics were first studied intensely by Helmholtz;⁹⁰ the theory he produced was later applied to electrophoresis by von Smoluchowski.²⁷⁵ The zeta potential and the electrophoretic mobility were shown to be related by the following equation;

$$v_e = \frac{E\epsilon\zeta}{4\pi\eta} \quad (9.1)$$

ϵ is the dielectric constant and η is the viscosity of the liquid.

(A detailed derivation of this equation is given in Kruyt,⁸⁵ p. 207.)

The em, v_e/E , is commonly recorded as $\mu\text{m s}^{-1}\text{cmV}^{-1}$ so that for ideal hydrosols at 25°C;

$$\zeta = 12.83 \frac{v_e}{E} \quad (\text{mV}) \quad (9.2)$$

The Smoluchowski equation (9.1) was derived from the linear form of Poisson's equation (4.8), i.e., where the Laplacian operator ∇^2 has been replaced by d^2/dx^2 . Thus (9.1) can only apply if the range of the potential of the particle, the thickness of the electrochemical double layer, $1/\kappa$, is much less than the radius of curvature of the surface, r_0 . The surface is then approximately planar and (9.1) holds regardless of the particle shape, i.e., $\kappa r_0 \gg 1$.

At low κr_0 when the particle is very small compared with its electric field it becomes necessary to use the three-dimensional form of the Poisson-Boltzmann distribution from which the Hückel equation has been derived;

$$v_e = \frac{E\epsilon\zeta}{6\pi\eta} \quad (9.3)$$

This case is uncommon as it holds only for $\kappa r_0 \ll 1$; for a 50 nm hydrosol the electrolyte concentration must be less than 10^{-7} M. Unfortunately most colloidal systems lie between these two limits.

Henry²⁷⁶ recognised the electrophoretic effect, the retardation

of charged particle movement by the opposing migration of its counter ions; an effect insignificant for large κr_0 but not for small. The equation he developed gives a continuous monotonic relationship of v_e with κr_0 between the two extremes of (9.1) and (9.3) for constant ζ . It has the form;

$$v_e = \frac{E\epsilon\zeta}{4\pi\eta} [1 + \lambda \text{fn}(\kappa r_0)] \quad (9.4)$$

where $\lambda = \frac{1}{2}$ for spheres and $\text{fn}(\kappa r_0)$ increases monotonically between 0 for small κr_0 and 1 for large.

A further important phenomenon which is particularly consequential for $0.2 < \kappa r_0 < 50$ is the relaxation effect. When a particle moves through an electrolyte under the influence of an electric field its own electrochemical region of interest, its double layer, loses longitudinal symmetry and this deformation as the diffuse layer reforms reduces the particle velocity. The influence is greatest when ζ is high, i.e., the double layer is most extensively developed. Both Overbeek²⁷⁷ and Booth²⁷⁸ produced equations for the v_e which incorporated both relaxation and electrophoretic effects but, because of simplifying approximations, both tend to overestimate the corrections.⁸⁶ More correct numerical solutions have been prepared by Wiersema et al.²⁷⁹ based upon the following assumptions:

- (i) the suspensions are dilute and the particles are independent,
- (ii) the particles are rigid non-conducting spheres with uniform charge distribution over the surface,
- (iii) the electrical permittivity of the particle and the solution, and also the latter's viscosity, are not functions of position,
- (iv) only one cation and one anion are to be found within the ionic atmosphere of the particle.

At low ζ their results approached those of Henry, (9.4), whilst Smoluchowski's (9.1) and Hückel's (9.3) equations are the limiting cases at high and low kr_0 respectively. Extension of the theory to include multivalent ions showed the greater effect of these upon mobilities than the univalent ions and also the greater influence of the counterions; the numerical results were less reliable.²⁷⁹

A final point, discussed fully by Dukhin and Derjaguin,⁸⁶ is the phenomenon of surface conductance or transfer of charge through the fixed layer along the surface. Where this occurs the em cannot be considered to be independent of the surface shape. If this is the case true zeta potentials can be determined only for well characterised spheres and not for irregularly shaped or porous particles. This is at variance with the Zeta Meter Manual²⁸⁰ which recommends conversion of electrophoretic mobilities to zeta potentials under all circumstances using (9.1) or (9.4) without recourse to more recent theories.

For ideal materials it can be seen that electrophoresis may be able to yield information of the nature of the electrochemical double layer. For non-ideal systems it will, however, still reflect the changes found within the fixed layer which are extremely important in colloid studies.

9.3 Electrophoretic Properties of Hydrous Oxides and Charge Reversal

The variation of the electrophoretic mobility of hydrous oxides with pH in simple indifferent electrolytes is generally symmetrical about the IEP. Below this pH the bodies are positively charged; above it they are negative. Increasing the concentration of indifferent electrolyte leads to a reduction in the magnitude of the em but retains the same IEP confirming that the zeta potential is indeed a diffuse layer potential. In general the IEP and the PZC in such

electrolytes are similar.^{88,123}

The adsorption of multivalent cations increases the apparent surface charge and the IEP of hydrous oxides; multivalent anions have the reverse effect. For a colloid with a relatively low IEP its em may be altered by adsorption, of cations especially, so that above its IEP it has a maximum negative mobility. Further increase of the pH induces greater cation adsorption at a rate in excess of the development of surface negative charge so the em becomes less negative and it may even become positive again. The electrolytic conditions for this apparent IEP is the point of charge reversal. With further pH rise there will be a maximum in the positive em above which the surface becomes more negative and there is a third apparent IEP. Charge reversals are generally found only with hydrolysing ions and, for cations, they may arise from surface deposition of the hydroxide. The IEP's at high pH correspond to mixed IEP's of the substrate and the adsorbed hydroxide; if the surface is covered by a monolayer of the hydroxide the IEP at highest pH is that of the hydroxide alone.¹⁰³ A similar charge reversal can be brought about by the adsorption of multivalent anions such as phosphate.¹⁷¹ The relative ability of a large number of ions to bring about charge reversal by such adsorption has been discussed by Wakatsuki et al.¹⁸⁷ The rôle hydrolysable ions play in electrophoresis was also elucidated by Matijević and co-workers (for a review see ref. 281).

9.4 Electrophoretic Properties of Clay Minerals

Clay particles, while amenable to electrophoresis because of their size range, 0.2 to 2 μm , do not lend themselves to interpretation of their mobilities in terms of their surface potentials or surface charge densities. The reasons for this include; their awkward size region for most electrolyte concentrations which

invalidates reasonable application of the simple equations, their shape which is seldom anything like spherical, and their surface conductance which can be appreciable.^{213,214} Furthermore, most clays, particularly those which are crystalline, have regions of quite different charge density and may even have regions of opposite charge.^{115,127,254,282} Any zeta potential calculated for the whole particle could not then be representative of the actual surface. For these reasons it is preferable to talk of the directly measured physical property, the electrophoretic mobility, rather than convert it to an approximate zeta potential.

As might be expected from their charging mechanisms, (4.7), the em of clays becomes more negative with increasing pH.^{132,283-285} In many cases such as with montmorillonite, kaolinite and halloysite, positive mobilities are not observed for the natural material suspended in 1:1 electrolytes above pH 3.^{127,132,136,285} The clay mineral imogolite is somewhat different in that at low pH it is strongly positively charged but it loses this charge upon neutralisation between pH 6 and 9 whereupon it has no nett charge.³⁵ In this respect imogolite acts in the reverse manner of silica which shows no positive mobility.^{286,287}

Allophane typically has sigmoid em/pH curves centred upon zero mobility, the IEP, between 5.5 and 7.2 depending upon the material and its pretreatment.^{35,36,140,141} (Some representative IEP's are given in Table 5.2.) These treatments include; air drying which reduced the IEP from 6.2 to 4.1 in one instance¹⁴¹ but made no change in another³⁵ although the absolute mobilities were reduced; acid washing which raised the IEP from 5.8 to 7.3 by some unknown mechanism;³⁵ and hydrolysable ion adsorption, e.g., of copper and phosphate,³⁶ which has profound effects not only for clays but for all hydrosols. Adsorption of aluminium in particular decreases negative,

and enhances positive, $\epsilon_m^{127,136,285,288,289}$ even at concentrations as low as 10^{-6} M. In addition, its removal from clays by acid washing enhances negative mobility by making the surface more siliceous¹³² silanol (Si - OH) being readily deprotonated and negative charge bearing except at very low pH.

Milestone found the IEP of some Waikato allophanes were reduced when they were subjected to processes which removed hydrous iron(III) oxide components.¹¹ This was said to show the importance of iron to the colloid properties of allophane but the possibilities of removal of aluminium or adsorption of components of the iron removing agents, which could have the same effect, were not considered. (The absolute values of the IEP's obtained by Milestone¹¹ must be interpreted with care. He used a crude apparatus made from two thin strips of platinum foil mounted upon a microscope slide between which a suitable suspension was placed and covered with a cover slip. No consideration of electro-osmosis was made and this would have been difficult as the cell thickness was unknown and probably non-uniform; additionally, bulk fluid flows from capillarity or from electrolysis were neglected except when visible to the naked eye. All these influences can give inaccurate results.)

9.5 Experimental Studies

9.5.1 Methods and Materials

The electrophoretic mobilities of colloidal suspensions were measured with a Riddick Zeta-Meter (supplied by Zeta Meter Inc., N.Y.) incorporating a perspex cell with a molybdenum anode and a platinum-iridium cathode. The voltage to be applied was determined, after measurement of the suspension's specific conductance, by consultation of the table supplied with the apparatus. (At higher conductivities associated with moderate electrolyte strengths if

excessive voltages are applied the energy lost by internal friction induces thermal convection of the cell contents and consequently the colloids cannot be tracked.) The movements of the particles were followed through a stereoscopic microscope along a line distant $14.7\% \pm 1\%$ of the tube diameter from a side. At this point the net liquid flow from electro-osmosis at the cell wall was zero. The times required for each of between 5 and 15 particles to travel over a predetermined distance were recorded and after averaging these were converted to em using the nomograph also supplied in the manual.²⁸⁰

The samples were taken either from the titration experiments (see section 5.4.4) or prepared specifically in a similar manner. The "fresh" samples were prepared by the addition of one or two drops of near neutral clay suspension (5 to 10 g l^{-1}) to the supernatant liquid obtained from centrifugation of a larger volume of the suspension (20 to 30 ml) and the pH adjusted to a suitable value by the addition of either dilute hydrochloric acid or sodium hydroxide. The em was measured within two hours. In all cases the pH was recorded immediately prior to electrophoresis as described in section 5.4.4.1. In no case was the sedimentation of particles found to interfere with the determinations.

9.5.2 Results

The em found for Ohaupo allophane (in the sodium form) is given in figure 9.1 as a function of pH for three different concentrations of sodium chloride. The clay had an apparent IEP of 6.3; it was positively charged at lower pH and negatively charged in more basic solutions. The change in the mobility was roughly linear near the IEP but it was reduced at the pH extremes. An increase in the strength of the electrolyte brought about a reduction in the absolute mobility. The aluminosilicate showed similar electrophoretic

characteristics to the allophane above except that it did not appear to have a maximum em at low pH and it had a different IEP. The em of the fresh Mangawara halloysite was found to vary to a lesser extent with electrolyte strength (fig. 9.3); the higher concentration apparently induced a more negative total charge. The particles in this instance were negatively charged over the complete range of study, i.e., pH 2.5 to 10, with a monotonic increase with pH. Ageing of this clay as a 7.2 gl^{-1} suspension at various acidities induced significant changes at pH less than 5 with the greatest change being observed for the most dilute electrolyte (fig. 9.4). In all cases a charge reversal occurred and the particles had a nett gain of positive charge.

To investigate the influence of the dithionite-citrate process, described in section 3.9, upon the electrophoretic properties of allophane and the aluminosilicate, samples of these colloids were subjected to not only the complete treatment but also to the cold citrate reagent and the cold dithionite reagent as well. The em of each of the materials after these treatments is shown in figure 9.5, for the aluminosilicate, and figure 9.1 for the allophane. In all cases these treatments lead to a substantial increase in the negative charge component of each material; furthermore the changes were approximately the same irrespective of the treatment.

9.5.3 Discussion

A different representation of the charge characteristics of allophane to that obtained by titration is shown by the em/pH interrelationship depicted in figure 9.1. Again the charge changed continuously from positive at low pH to negative at high as a result of protonation and deprotonation reactions, respectively. The effects of the permanent negative charge are not so apparent here

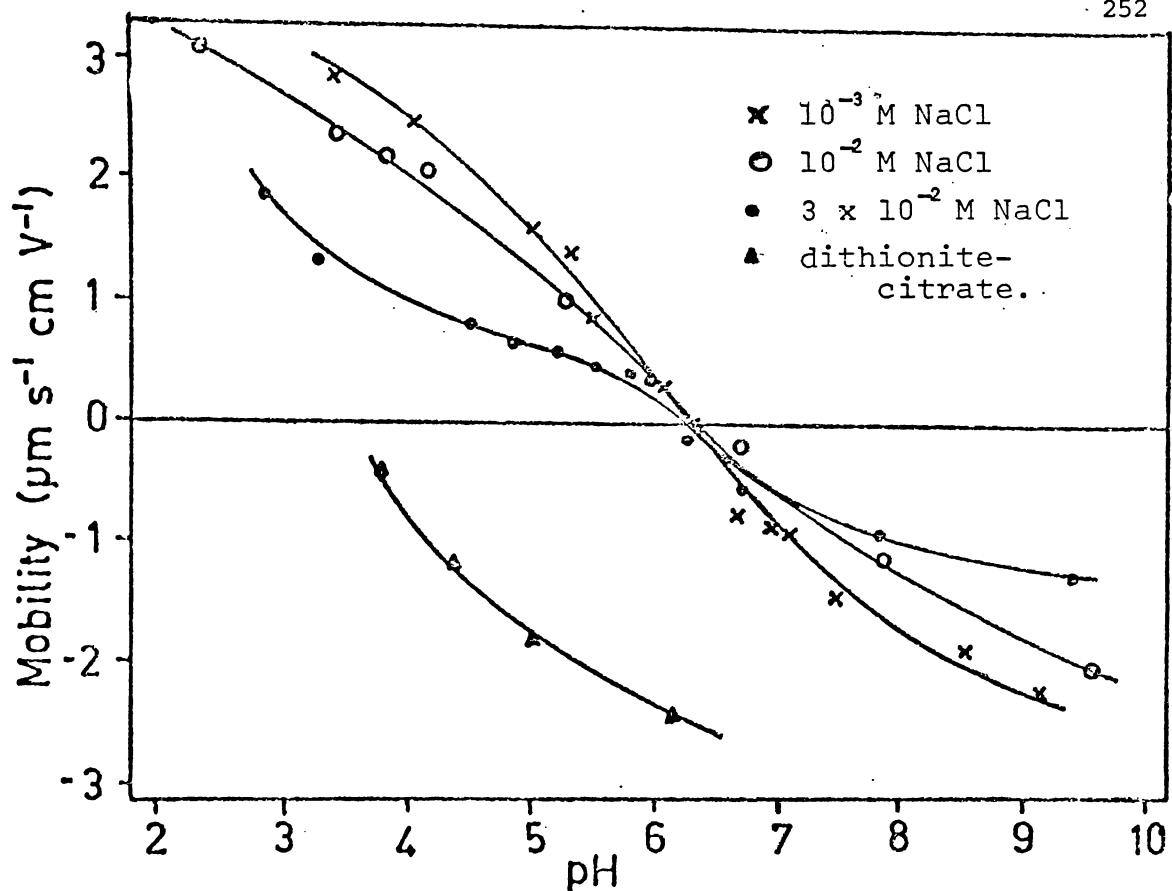


Figure 9.1. Electrophoretic mobility of Ohaupo clay as a function of pH and electrolyte concentration.

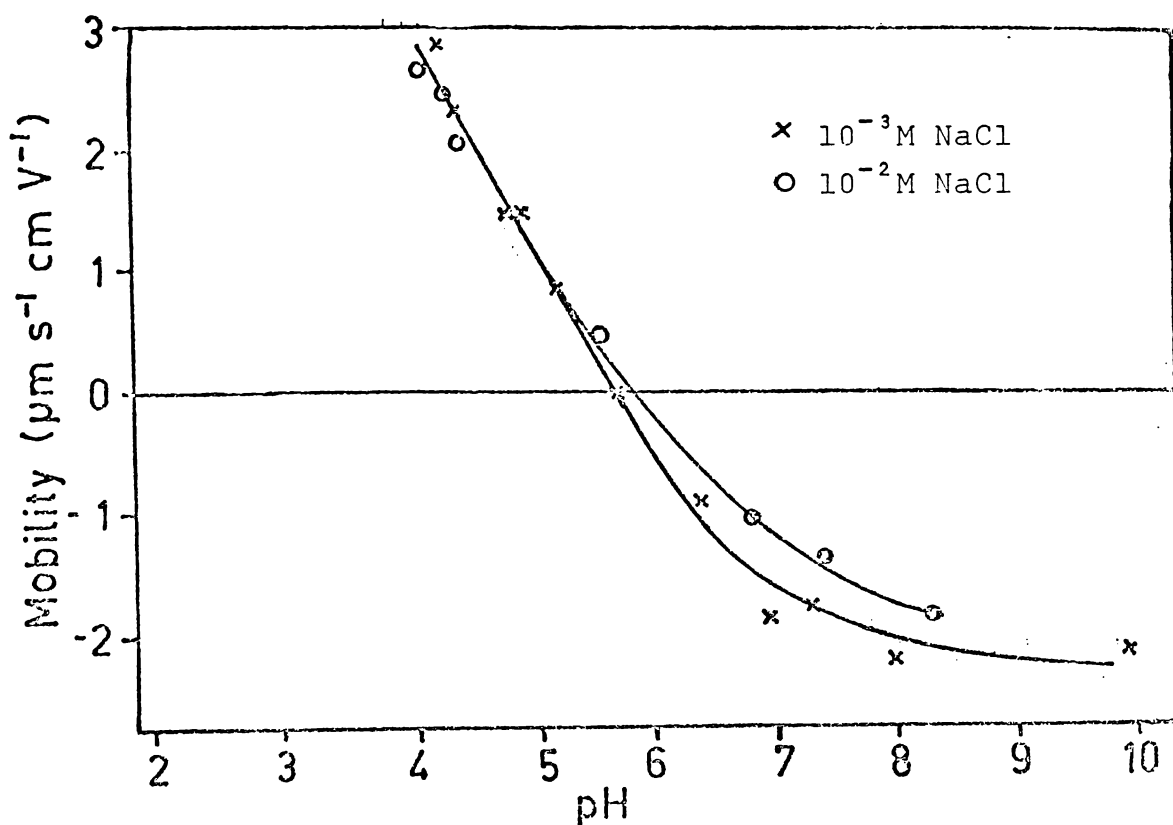


Figure 9.2. Electrophoretic mobility of a synthetic aluminosilicate as a function of pH and electrolyte concentration.

because the clay had been aged and so all permanent charge neutralisation sites would have been occupied by cations other than H^+ , most particularly aluminium which, because of its ability to hydrolyse readily, would enter into the surface charging reactions itself. The decrease in the absolute em with electrolyte concentration was a result of the reduction in the effective electric potential felt beyond the fixed layer. This was caused by the greater amount of charge neutralisation that occurred within the fixed layer leading to a reduction in the counterion charge needed in the diffuse layer. The sigmoid shape shows limits to the em of about $3 \mu m s^{-1} cmV^{-1}$; this is common with clays but not with hydrous oxides.^{127,132,136,283} The allophane isoelectric point at 6.3 was about 1.4 units higher than its PZC determined by titration. Whilst the discrepancy may in part be due to permanent negative charge influences on the PZC, it was also similar to the effect observed for IEP and PZC determinations in the presence of a specifically adsorbing multivalent cation. (This would decrease the PZC and raise the IEP.) The most likely cation present here that might have this effect was aluminium but when the PZC was determined for an allophane from which some surficial aluminium had been removed by acid washing its PZC did not increase, a result which suggested that the aluminium was more a part of the mineral matrix rather than a specifically adsorbed cation. From the cation adsorption experiments it was found that when significant amounts of this element were present in solution it was able to adsorb and occupy cation adsorption sites at the expense of less firmly binding cations such as sodium and calcium. Thus this element is not only a matrix component but also an adsorbed species and as such it may be responsible for the influences seen here.

There is yet a component of the allophane which has not been

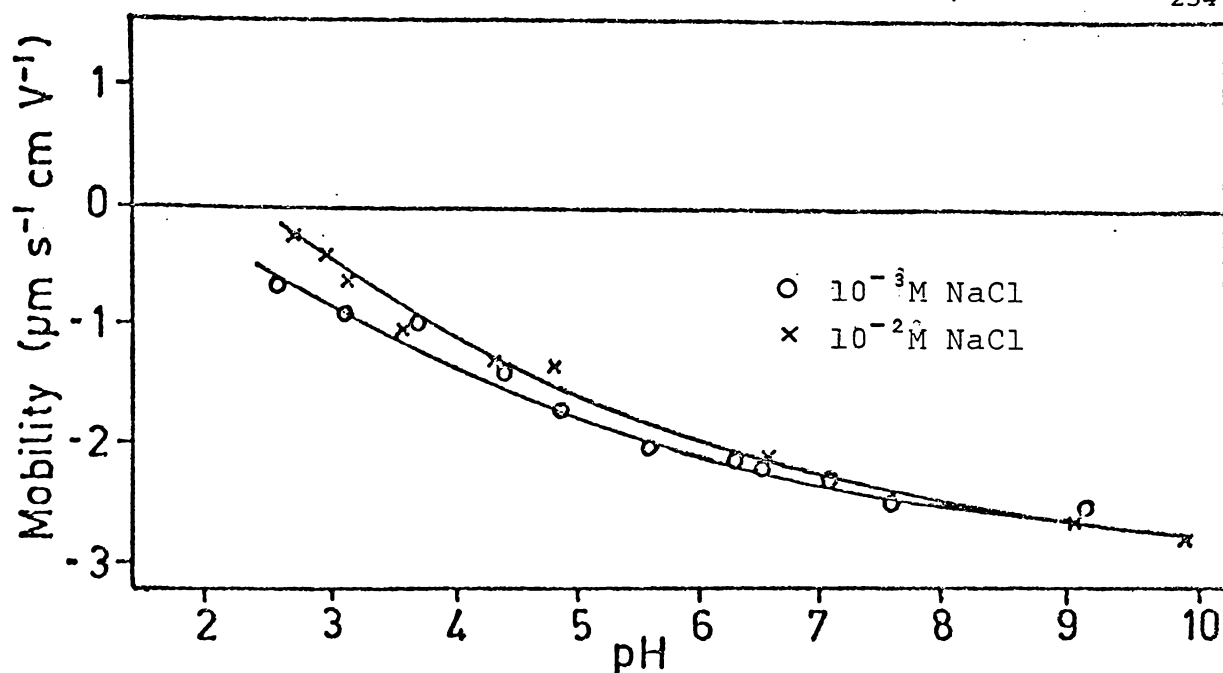


Figure 9.3. Electrophoretic mobility of Mangawara clay (fresh preparation) as a function of pH and electrolyte concentration.

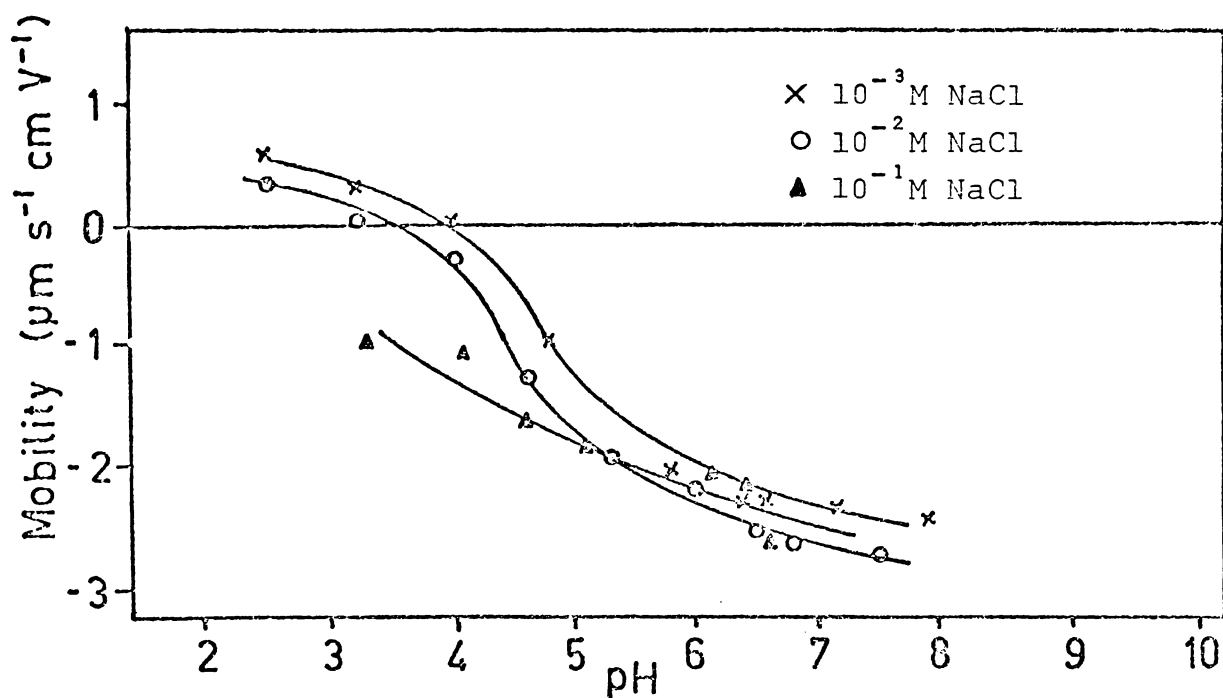


Figure 9.4. Electrophoretic mobilities of Mangawara clay (acid-aged preparation) as a function of pH and electrolyte concentration.

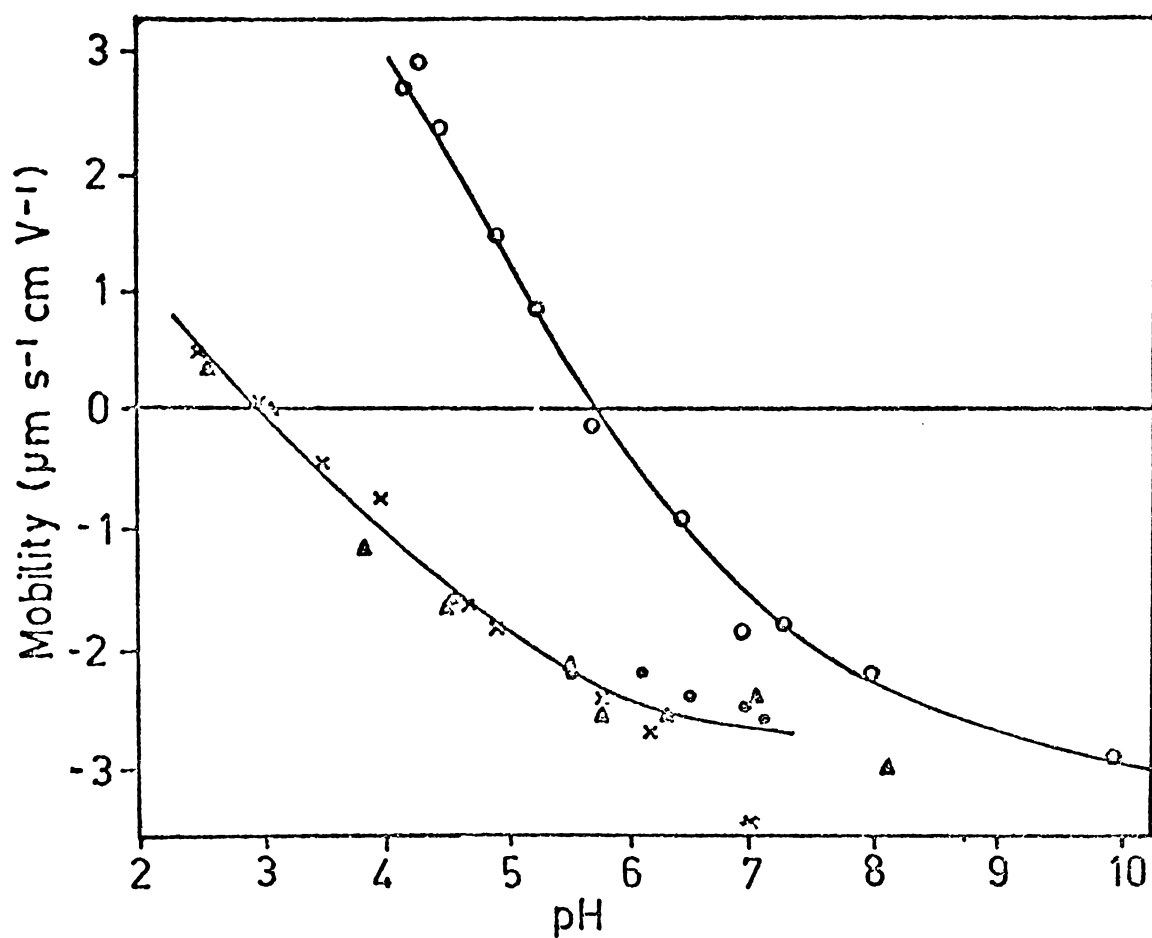


Figure 9.5.

Electrophoretic mobilities of a synthetic aluminosilicate after treatment with various reagents.

○ no treatment; ▲ full treatment;
 x cold citrate only; • cold dithionite reagent only.

considered. Iron(III) hydrous oxides are present in the clay and make up about 5% of the total mass. It is thought that the iron exists predominantly as discrete particles probably adsorbed onto the aluminosilicate part of the mineral¹¹ so that the total colloid presents a surface of aluminosilicate (negative charge tendencies) and iron(III) and aluminium hydrous oxides (positive charge tendencies). Whilst this amount of iron(III) may have large effects upon the electrokinetic properties its effect on the surface charge characteristics would be relatively slight.¹³¹

When the allophane and the aluminosilicate had the opportunity to interact with the dithionite-citrate or either of the component reagents they both lost or had blocked a large proportion of the positive charge contributing component. Whilst this process has been widely used to remove free iron(III) oxides from soils and clays it also removes substantial amounts of aluminium.²⁸³ So too does the citrate reagent alone.^{204,283} These all lead to an increase in the surface negative charge.¹³⁸ After these reactions the surface was left resembling a well leached aluminosilicate like halloysite or kaolinite. As the various reagents have the same effect upon the aluminosilicate and the clay it is likely that the high positive charge component on each could be attributed to the octahedral aluminium. In allophane the iron(III) component would only supplement this charge.

The em of the Mangawara halloysite was similar to its more highly crystalline relative, kaolinite, with its low IEP. An actual IEP was not found here but it would be less than 2.5. With pH increase above this point negative charge density increased slowly also like that of kaolinite.^{132,285} The apparent charge density was much reduced at low pH because of the large permanent negative charge that needed to be neutralised before the particle could become

positive but as this was not readily achieved halloysite would only display a positive em under strongly protonating circumstances or because of adsorption of multivalent cations. On ageing in relatively concentrated suspensions at low pH a charge reversal occurred. The cause of this was the dissolution of aluminium from the matrix and its adsorption back onto the mineral surface at cation adsorption or permanent charge neutralisation sites. Wakatsuki *et al.*²⁸⁵ have shown that charge reversal of very dilute kaolinite suspensions at pH 5.9 to 6.3 can be induced by an aluminium concentration of 10^{-6} M. (This is close to solution saturation with respect to precipitation of the hydroxide and so large effects might be expected in dilute systems. In fact many of their results can be interpreted in terms of surface coatings of the adsorbed metal hydroxide.) The aluminium concentrations found in suspensions of similar composition and pH, but after only one day of stirring, to those being discussed here are shown in figure 8.1; at pH 3 for instance, the aluminium concentration was 3×10^{-5} M. It is notable that the region where aluminium solubility was significant, ($> 10^{-6}$ M) below pH 5, coincides with the region of change in the em upon ageing. Hall²⁸⁸ has shown that, for a kaolinite suspension, for the same aluminium concentration the em had a maximum at pH 5 to 6 where adsorption was sufficiently high to induce a large site occupation. The lack of a maximum here will be due to the variable aluminium concentration; at lower pH the concentration was higher, more aluminium sorbed and so the colloid charge and zeta potential were more positive than at higher pH. The effect of an increase in the electrolyte concentration here was the reverse of that anticipated from electrophoretic considerations. The concentration of the background electrolyte had little influence upon the amount of aluminium dissolved (fig. 8.1) but it did interfere with its surface

adsorption (see section 8.3.5) again in a manner similar to that on kaolinite.¹³⁵ Thus at higher electrolyte concentrations the em is more negative because of reduced adsorption of aluminium.

If iron(III) was a significant source of positive surface charge for these clays then it should also be apparent in this halloysite which contained 4.8% Fe_2O_3 by weight. This is only 0.9% less than the Ohaupo clay (section 3.9). As the em/pH curve for the fresh halloysite was very similar to that of the dithionite-citrate treated aluminosilicate it is clear that the iron(III), in this material at least, played little part in its electrokinetics.

9.6 Conclusion

The electrophoretic mobility of allophane changes monotonically from its IEP, becoming more positive with decreasing pH and more negative with increasing pH. The magnitude of this mobility also decreased with the concentration of indifferent electrolyte in much the same manner as for the hydrous oxides. Ohaupo allophane (in the sodium form) had an IEP near pH 6.3 in sodium chloride solution. The high value of the IEP means that in soils particularly, and in many natural water systems, allophane will have only a low nett charge which may be positive or negative. This sets it apart from the other colloids found in these environments, especially microorganisms, humic materials and the other common clay minerals, which are all highly negatively charged. In the next five chapters some aspects of the surface and colloid chemistry of allophane that are influenced by this property will be discussed.

In fresh suspension the Mangawara halloysite displayed electrophoretic characteristics like those of kaolinite, i.e., an IEP below pH 3 and a negative charge which increased with pH. Upon ageing in acid, aluminium transferred from the matrix to cation adsorption sites

blocking negative charge. The amount transferred was dependent upon the pH and the concentration of the electrolyte. High concentrations of sodium inhibited the exchange by competing successfully for adsorption sites. The transfer was sufficient to cause charge reversal in some situations and modified the properties of the halloysite towards those of allophane.

A synthetic aluminosilicate was found to have somewhat similar electrophoretic behaviour to allophane. When this material and the allophane were subjected to the dithionite-citrate process used for the removal of hydrous iron(III) oxides they became much more negatively charged and like the halloysite. The halloysite and the allophane both had similar quantities of hydrous iron(III) oxide but widely different IEP's. As the dithionite-citrate reagent is also able to remove free aluminium hydrous oxides it is probable that it is this component, and not the iron(III) species, that gives allophane its high IEP. Any surface charge interactions displayed by iron(III) species in allophane would be complementary to those of the hydrous aluminium material. These results reaffirm the words of Saunders²⁹⁰ who stated that as the dithionite-citrate reagent is not specific for iron(III) it "should not be used uncritically in studies of soil colloids".

CHAPTER TEN

THE STABILITY OF ALLOPHANE SUSPENSIONS

10.1 Introduction

Flocculation is an important and common process in colloid chemistry by which particulate dispersions in liquids can be aggregated to form larger bodies. These have a sufficiently large mass to sediment under the influence of gravity, when the individual units may not (see section 3.7). The mechanism by which a dispersion may be destabilised, i.e., become susceptible to flocculation, is dependent upon the nature of the forces acting between the bodies when they collide as a result of diffusion or Brownian motion. To understand these processes a knowledge of the types of interaction that occur upon close approach is necessary. These interactions will be considered, first for similar particles of the same material and then for particles of different composition and size. A resumé of the flocculation of other clay minerals will follow and finally the results of an experimental study and a discussion of the effects of simple electrolytes upon the stability of suspensions of an allophane will be presented.

10.2 The Interaction between Like Particles

There are three major types of interaction involved when two similar colloidal particles approach one another, namely:

- (i) the attractive London-van der Waals forces,
- (ii) the repulsive Coulombic forces,
- (iii) the steric forces arising from the presence of adsorbed material at the surface.

The first two of these form the basis for the classical theory of flocculation and stabilisation of dispersions first proposed by Derjaguin and Landau²⁹¹ and later independently by Verwey and Overbeek.²⁹² This is now known as the DLVO theory.

10.2.1 London-van der Waals Attractive Interactions

The London-van der Waals forces are electromagnetic and are due to spontaneous transient electric polarisations arising from molecular distortions and orientations as well as electron motions. These cause spontaneous perturbations of the electronic systems of the atoms of nearby bodies and result in attractive forces between them. For atoms these forces are quite small except over very short distances as they decay inversely with the sixth power of the interatomic distance. For macroscopic collections of atoms, however, the distances over which these forces are operative, i.e., comparable to or in excess of repulsive forces, may be of the order of colloidal dimensions. The magnitude of the interaction has been calculated from optical data or, as originally, by assuming that the London forces for atoms were additive.^{293,294} It has also been determined experimentally.²⁹⁵ As with diffuse layer calculations the equation describing the interaction energy is dependent upon the relative particle radius.

The attractive energy, V_A , between two particles increases with their diameter and density. It decays with the sixth power of the

separation for large distances but for short distances the decrease is much less.

10.2.2 Coulombic Interactions

That suspensions of a single colloid particle type in dilute aqueous electrolytes can be stable (i.e., the number of particles does not change with time), means that they must experience some force greater than the attractive London-van der Waals forces which would aggregate them and cause their sedimentation. This stability arises solely from electrostatic repulsions of the charges borne by the particles which originate in the manners described earlier. As a consequence of electroneutrality each particle has about it an atmosphere of counter charges which form, together with the surface charge, the double layer. The distribution of this counter charge has profound effects upon the interparticle coulombic attraction. On migration of two particles towards each other as a result of Brownian motion or suspension agitation when the diffuse layers are extensive they will interpenetrate at large distances, the electrostatic fields will overlap and the repulsion will be effective. Compression of the double layer means that the particles will be much closer before the repulsion will be significant and so the London-van der Waals forces may dominate and cause aggregation.

In the original DLVO theory the double layer structure assumed was that of the Gouy and Chapman (see section 4.5.2). The rôle of the Stern layer has been shown to be important in predicting the rôles played by the ions of the electrolyte.^{100,296} Clearly the more exact the ion distribution theory the more reliable the predictions will be. The use of this distribution theory is not unreasonable if the operative surface potential is the potential of the OHP, ψ_d , or alternatively the zeta potential, ζ ,²⁹⁷ in which case the effects

within the Stern layer and at the surface will both be included. Upon interaction there must be a reorganisation of the double layer between the particles. It is still a matter of conjecture which of the factors associated with the double layer, if any, can remain constant. With rapid interaction ionic desorption would be unlikely and so the surface potential would be forced to alter. If the interaction was suitably slow surface and Stern layer charges could be rearranged but this is rare as high exchange currents are unavailable on many surfaces.²⁹⁸ Although the DLVO theory was developed for constant potential systems the differences for constant charge systems are not great. For constant potential the repulsive energy, V_C^ψ , for potentials less than 50 mV is given by;

$$V_C^\psi = \frac{\epsilon r_o \psi_o^2}{2} \ln(1 + \exp(-\kappa H_o)) \quad (10.1)$$

The superscript refers to the factor remaining constant and ψ_o is the operative surface potential, $\psi_o = \psi_d$ or ζ . r_o is the particle radius, H_o is the distance between them and $1/\kappa$ is the Debye parameter. For constant surface charge;

$$V_C^\sigma = \frac{V_C^\psi - 2\epsilon r_o^2 \psi_o^2}{2r_o} \ln(1 - \exp(-2\kappa H_o)) \quad (10.2)$$

Experimentally determined energies lay between these two with greater similarity to the constant charge value.²⁹⁷

The repulsive energy increases with the operative potential and decreases with increasing particle radius, interparticle distance and electrolyte concentration.

10.2.3 The total Interaction between Like Particles

The total energy of interaction, V_T , is usually taken as the sum of the various components;

$$V_T = V_A + V_C \quad (10.3)$$

The repulsion varies almost exponentially with separation, has a range of the order of the double layer thickness and remains finite for all separations. The attractive energy decreases with an inverse power of the separating distance and becomes exceedingly large (negative) for close approach. At short and large distances the attraction will predominate but for intermediate distances there may be a nett electrostatic repulsion. In figure 10.1 the energy curves for some interactions are presented. The primary minimum at close approach and the secondary minimum at a distance of the order of the double layer thickness are obvious. The increase in V_T for very small distances results from actual contact of the particles and their surface orbital overlap.

Flocculation proceeds when bodies can combine to form a unit sufficiently large to be unaffected by the Brownian motions. For this to happen either the potential energy barrier, $V_{\max}$, must be small with respect to kT , the thermal energy associated with Brownian motion, or the secondary minimum must be much deeper than kT . In the first situation the particles lie close together whilst in the second they are separated by some layers of solvent. There is a trend to calling the first situation coagulation and the second flocculation; this distinction is not made in this thesis.

Both V_C and V_A are approximately proportional to r_0 so that flocculation induced by the secondary minimum will be more important for larger bodies and increased electrolyte concentrations. A system which has flocculated in this way is generally reversible and can be readily redispersed.

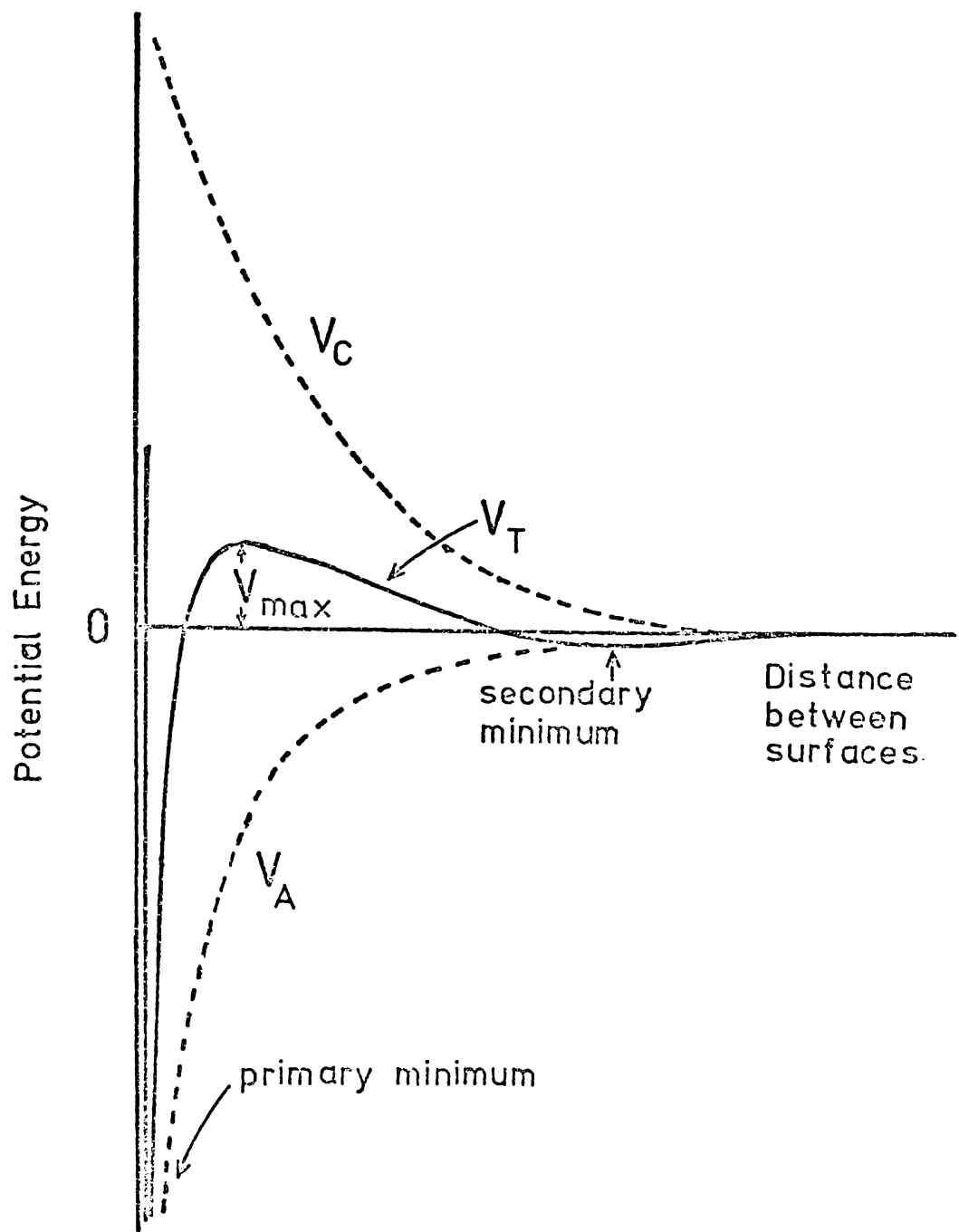


Figure 10.1. Potential energy curves for the interaction of two charged surfaces.

10.2.4 Flocculation Kinetics

There are two flocculation rates of interest. The first is the maximum rate which is diffusion controlled and occurs when the nett interparticle forces are zero except at approach close enough to ensure coalescence. The second is the rate for flocculation in the presence of a potential barrier, i.e., it is diffusion in a force field.

For the maximum rate, as the coalescence is a binary process, the change in the total number of particles N is;

$$-\frac{dN}{dt} = k'N^2 \quad (10.4)$$

where k' is the rate constant. Integration of (10.3) if $N = N_0$ at time $t = 0$ gives;

$$\frac{1}{N} = \frac{1}{N_0} + k't \quad (10.5)$$

Smoluchowski's equation for the frequency of collision, I , between particles at $t = 0$ is;

$$I = N_0^2 k' = 8\pi D r_0 N_0^2 \quad (10.6)$$

where D is the diffusion coefficient which can be obtained from Einstein's equation;

$$D = \frac{kT}{6\pi\eta r_0} \quad (10.7)$$

where η is the fluid viscosity. Thus;

$$\frac{1}{N} = \frac{1}{N_0} + \frac{4kTt}{3\eta} \quad (10.8)$$

so that the inverse of the total number of particles is linear with time.

In the presence of a force field the rate will be decreased if a potential energy barrier is set up. This leads to the inclusion of a stability factor W related to the energy barrier height;

$$W = k'_0/k' = 2 \int_2^\infty \exp(V_T/kT) \frac{dS}{S^2} \quad (10.9)$$

i.e., the ratio of the rate constants for rapid and slow flocculation as k'_0 is the rate constant for $V_T = 0$. S is defined by

$$S = (H_0 + 2 r_0)/r_0 \quad (10.10)$$

If the flocculation of a dispersion is allowed to proceed without interference after the initial mixing there frequently remain slowly settling residual fine flocs after the main part of the suspendoid has descended. Agitation, which maintains the initially formed flocs in suspension, for a period after the mixing results in the formation of larger flocs and more efficient separation. Von Smoluchowski (see ref. 85) investigated the collision frequency expected between particles of type i and type j under the influence of a laminar current and derived the expression;

$$J = \frac{4}{3} N_i N_j R_{ij}^3 \frac{du}{dz} \quad (10.11)$$

where J is the collision frequency, N_i and N_j are the number concentrations of particles of type i and j respectively, R_{ij} is the collision radius and du/dz is the local velocity gradient. For the same particles the frequency of collision from Brownian motion is;

$$I = 4\pi D_{ij} R_{ij} N_i N_j \quad (10.12)$$

The mutual diffusion coefficient D_{ij} is given by;

$$D_{ij} = \frac{2kT}{3\pi\eta R_{ij}} \quad (10.13)$$

Comparison of (10.11) and (10.12), the two collision frequencies, gives;

$$\frac{J}{I} = \frac{\eta R_{ij}^3}{2kT} \frac{du}{dz} \quad (10.14)$$

For small particles, about 10 nm diameter, it is found that agitation of the suspension has little effect. When the particles are about 1 μm diameter the effects are about equal but for larger particles, and flocs, stirring is an aid to efficient flocculation.

10.2.5 Solution Factors that Influence Stability

The attractive interaction between any colloid pair at constant temperature is constant but the coulombic energy is sensitive to changes in the nature and concentration of the electrolytes as these influence κ and ψ_0 in manners described previously. In general changes in the p.d. ion concentration are small with respect to the total electrolyte concentration and so they have little effect upon κ . For materials charged by the adsorption of H^+/OH^- changes in pH will influence κ only at the pH extremes but their influences upon ψ_0 are profound and small pH changes can readily cause stable dispersions to coagulate. pH stability plots for these sols tend to be symmetrical about the IEP, where $\psi_0 = 0$ and the flocculation rate is maximised. Outside a region about this point stability may be found.

The double layer thickness is related to the electrolyte valence and concentration, especially the counterion, and changes in both of these also influence stability; an increase in the concentration of indifferent electrolyte increases the pH region of instability approximately symmetrically. An increase in the counterion charge also dramatically increases the region of instability or, alternatively, lowers the concentration of electrolyte required for the same result,

(the Schulze-Hardy rule). A common term in colloid stability discussions is the critical coagulation concentration (c.c.c.) which is the minimum concentration of counterion required to initiate fast coagulation. For a wide range of lyophobic colloids, such as PVC latex and the silver halides, and also *E. coli* there is an approximate linear relationship between the logarithm of the c.c.c. and the counterion charge. Such an effect is consistent with the DLVO theory.

The Schulze-Hardy rule is not followed so definitely when there are strong interactions between the counterion and the surface; in particular adsorption into the Stern layer. As this type of adsorption changes the diffuse layer potentials it will change ψ_0 . For negatively charged sols the flocculating efficiency of monovalent cations follows the lyotropic series; i.e., $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. This series is the same as the preference shown by most hydrous oxides for these cations, and reflects the ability of these cations to neutralise negative surface charge sites. It is usually found that specific adsorption of cations, especially multivalent ones, moves the IEP to higher pH and so moves the point of maximum coagulation in this direction as well. Specifically adsorbing anions move the IEP to lower pH; these influences are analogous to those found for electrophoresis and illustrate the value of this simple technique in colloid stability studies.

The rôle hydrolysable cations play in coagulation of lyophobic colloids has been the subject of an extensive and successful study by Matijević and co-workers (e.g., refs. 175, 299-302). Much of this work was reviewed in 1972.²⁸¹ Partial hydrolysis enhances the ability of an ion to adsorb onto many surfaces, especially hydrous oxides. In some cases the adsorption effects are so strong that they could only be the result of highly charged polynuclear complexes.

If an initially stable negatively charged hydrosol is subjected

to increasing concentrations of a hydrolysing cation a number of changes take place. First, at low concentrations, the surface charge is neutralised and the suspension is destabilised. With further concentration increase the adsorption of the cation causes a charge reversal of the colloid which then becomes positive. If sufficient cation complex can adsorb the colloid may be restabilised as a positive dispersion whilst at high concentrations this dispersion will be destabilised by the reduction of the double layer thickness. At high surface coverages the colloid has surface properties of the precipitated hydroxide; consequently it has an IEP near the PZC of the hydroxide. With aluminium and iron(III) this occurs near pH 8 to 9. As the salts of these two metals hydrolyse readily in neutral and weakly acid systems they will both tend to be present as strongly adsorbing cationic species. In natural waters and effluents most undesirable colloids are negatively charged; interaction of these with hydrolysis products of the above metals at low concentrations can be expected to reduce their stability and result in their flocculation. The actual processes used in water treatment which utilise salts of these metals are somewhat more complex and make use of large voluminous flocs of their hydroxides. In this way contaminants may be coated with aluminium or iron(III) hydroxide and destabilised, enmeshed in the forming hydroxide floc or, like soluble pollutants, they may be adsorbed by the solid hydroxide and removed with its sedimentation.

The coagulation behaviour of silica, like its surface adsorption behaviour, is quite different from the lyophobic colloids and the hydrous oxides of the common hydrolysed metals such as titanium and aluminium. The latter group all coagulate most rapidly at their IEP's,¹²³ whereas finely divided silica in the same region may be stable; in fact the cation concentration needed to flocculate it was

found to increase as its IEP was approached.²⁸⁶ It was also discovered that at the c.c.c. for a variety of non-hydrolysing cations the number of surface protons replaced by adsorbing cations had the same relationship with pH.¹⁹¹ It was suggested that ion exchange processes which remove silanolic protons are the primary factors controlling silica stability. These surface groups cause extensive water coordination and dispersion stability; replacement of the proton by a cation causes dehydration of the colloid and destabilisation of the dispersion.

The addition of organic liquids such as acetone or ethanol to aqueous dispersions is used commonly in clay chemistry to induce flocculation and assist collection of the dispersed phase. The flocculation is brought about by the reduction in the dielectric constant of the medium which in turn reduces the solubility of the various ionic components. Thus charge differentiation at the surface is much less pronounced, the effective surface potential is decreased and the stabilising coulombic interaction is less efficient.²⁹⁸

10.2.6 Influence of Adsorbed Polymers on Stability

The presence of an adsorbed layer of a surface active material, usually a polymer or macromolecule, at the solid/liquid interface may have profound effects upon colloid dispersion stability. By such adsorption dispersions may become extremely stable or they may be sensitized to flocculation. These effects find use in many technologies such as mineral separation, water purification and paint manufacture to name but a few.

Stabilisation by polymer adsorption can occur by two processes. In steric stabilisation a barrier is inserted between approaching particles which prevents contact that could lead to coalescence. When the polymer is a long chain, approach of another body will

interfere with its gyrations and compress it leading to a loss of freedom and a significant entropic repulsion. The greater the freedom of the polymer movement the greater the stability that ensues. Polymer freedom is enhanced if it is highly soluble in the dispersing medium; this however means weak adsorption so that very high polymer concentrations would be required. Block co-polymers of a lyophilic part (solvent attractive) and a lyophobic component (solvent repelling and usually strongly adsorbed on insoluble materials) then find frequent application as stabilising agents.

If the adsorbate is an ionic material such as a protein, starch or a polyelectrolyte it may protect a colloidal dispersion against flocculation, if complete coverage of the surface occurs, by enhancement of the Coulombic repulsion as well as by the steric effect. In many ways a coating of a polymer over a colloid gives that colloid aggregation properties similar to that of the dispersed polymer.

When only small quantities of stabilising agent are added to a dispersion, enough to coat only a small fraction of the colloid, flocculation may be induced by mutual adsorption of the polymer to two particles. Thus a polymer in the mg l^{-1} concentration range may induce flocculation but at the g l^{-1} range it acts as a stabiliser. The initial step at very low concentration involves polymer adsorption onto the colloid in insufficient numbers to form bridges and so the properties of the dispersion are little changed. At moderate concentrations interparticle bridging induces flocculation whilst at high concentrations the particles are completely coated with polymer and the dispersion is stabilised. Flocculation under these conditions does not proceed according to the DLVO theory but by this bridging mechanism instead. Coulombic interactions will occur if the polymer bears an electric charge. Depending upon the charge signs it may be nett repulsion or attraction; attraction between polymer and colloid

of opposite sign and repulsion between adsorbed polymer and adsorbed polymer or colloid if they have the same charge. A final interesting note is that prolonged and vigorous agitation of these flocculating systems can lead to a reduction in the flocculation efficiency. This may be because the free parts of the adsorbed polymer also become attached to the surface and no longer are available for bridging.³⁰³ Further discussions of the effects of polymers upon flocculation can be found in references 297, 298, 304-306.

10.3 The Interaction of Unlike Particles or Heterocoagulation

The interaction between two dissimilar particles that leads to their mutual coagulation is termed heterocoagulation. Again the same forces are involved in the interaction; i.e., the London-van der Waals and the Coulombic interactions.

The London-van der Waals attractive energy is dependent upon the nature of the material, the relative sizes of the particles and their separation

The Coulombic interaction energy for different particles depends upon the effective surface potentials of each. ψ_{01} and ψ_{02} . If these are of opposite sign the interaction is attractive; if they are similar the interaction is repulsive. With large differences between these potentials, even if they are of the same sign, the nett Coulombic interaction may be attractive³⁰⁷ (see fig. 10.2).

The total interaction energy, $(V_T)_{12}$ is again the sum of the components. It is found that the potential energy barrier that must be overcome to allow adhesion at the primary minimum depends mostly upon the particle with the smaller radius and/or potential.

The overall stability ratio, W_T , for the mixture, the inverse of the probability of a collision between particles of types 1 and 2 leading to adhesion, is;³⁰⁸

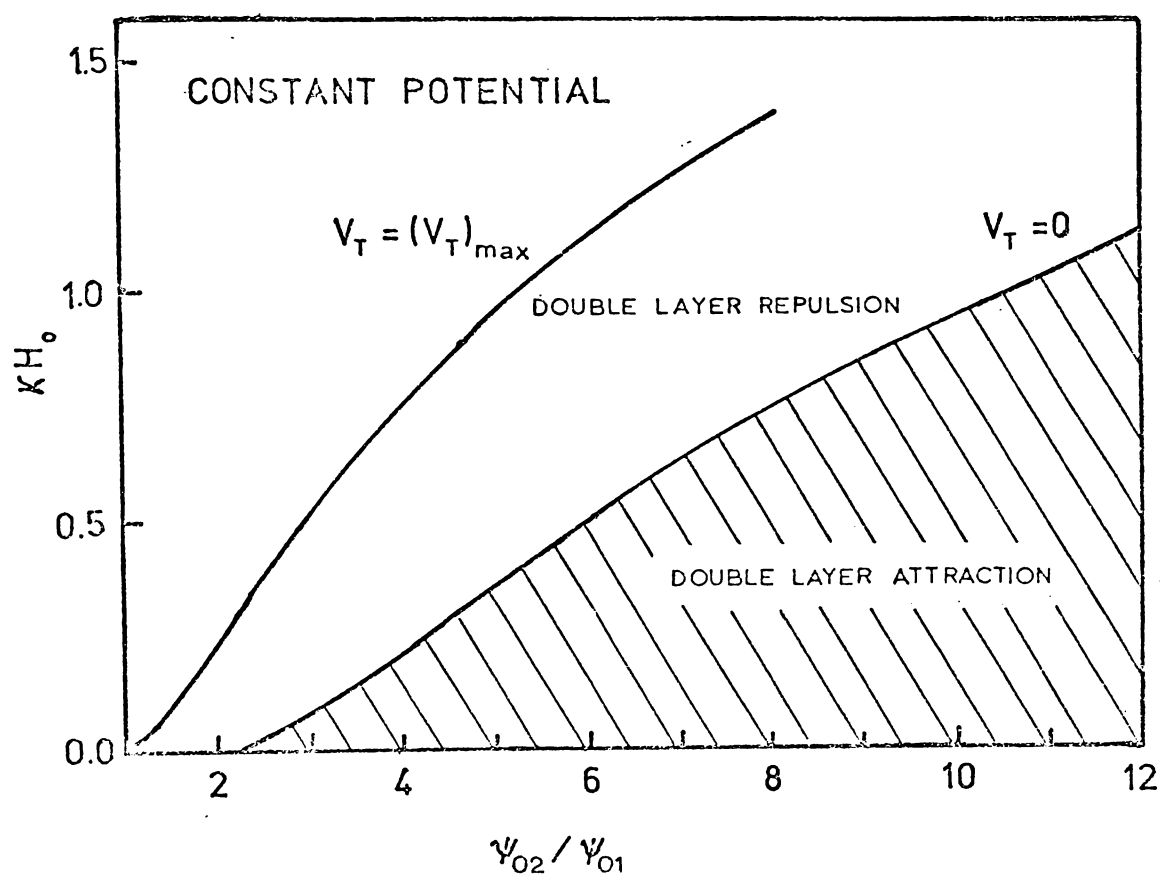


Figure 10.2. Values of κH_0 at which $V_T = (V_T)_{\max}$ and $V_T = 0$ as a function of the ratio of the effective surface potentials, ψ_{01}/ψ_{02} . (Redrawn from ref. 307.)

$$\frac{1}{W_T} = \frac{n_1^2}{W_{11}} + \frac{n_2^2}{W_{22}} + \frac{2n_1n_2}{W_{12}} \quad (10.15)$$

where $n_1 = N_1/(N_1 + N_2)$, $n_1 + n_2 = 1$, W_{11} and W_{22} are the stability constants for the homocoagulation of colloids 1 and 2 in isolation and W_{12} is the stability ratio for the heterocoagulation of colloids 1 and 2 defined by;

$$W_{12} = 2 \int_2^{\infty} \exp((V_T)_{12}) \frac{dS}{S^2} \quad (10.16)$$

The variation of the calculated stability ratio with pH for two colloids of similar radius but substantially different IEP, and hence surface potential, at various electrolyte concentrations is shown in figure 10.3. Mutual flocculation proceeds over the complete range between the two IEP's. The increase in the rate with decreasing electrolyte is a result of the extent of the double layer which, being large, permits attractive interaction over distances in excess of the range of the London-van der Waals forces especially for very small particles.

Experimental verification of the qualitative predictions of this theory have been presented by Healy *et al.*³⁰⁹ for the mutual coagulation of the oxides of tin and aluminium as well as those of titanium and aluminium, and also by Bleier and Matijević³⁰⁷ for PVC latex and monodispersed chromium hydroxide.

10.4 Colloid Stability of Clay Suspensions

The flocculation of the layer clay minerals such as montmorillonite and kaolinite differs from that of ideal homogenous materials usually used for flocculation studies because of the variation of charge distribution across the clay particle. The positive charge accumulation

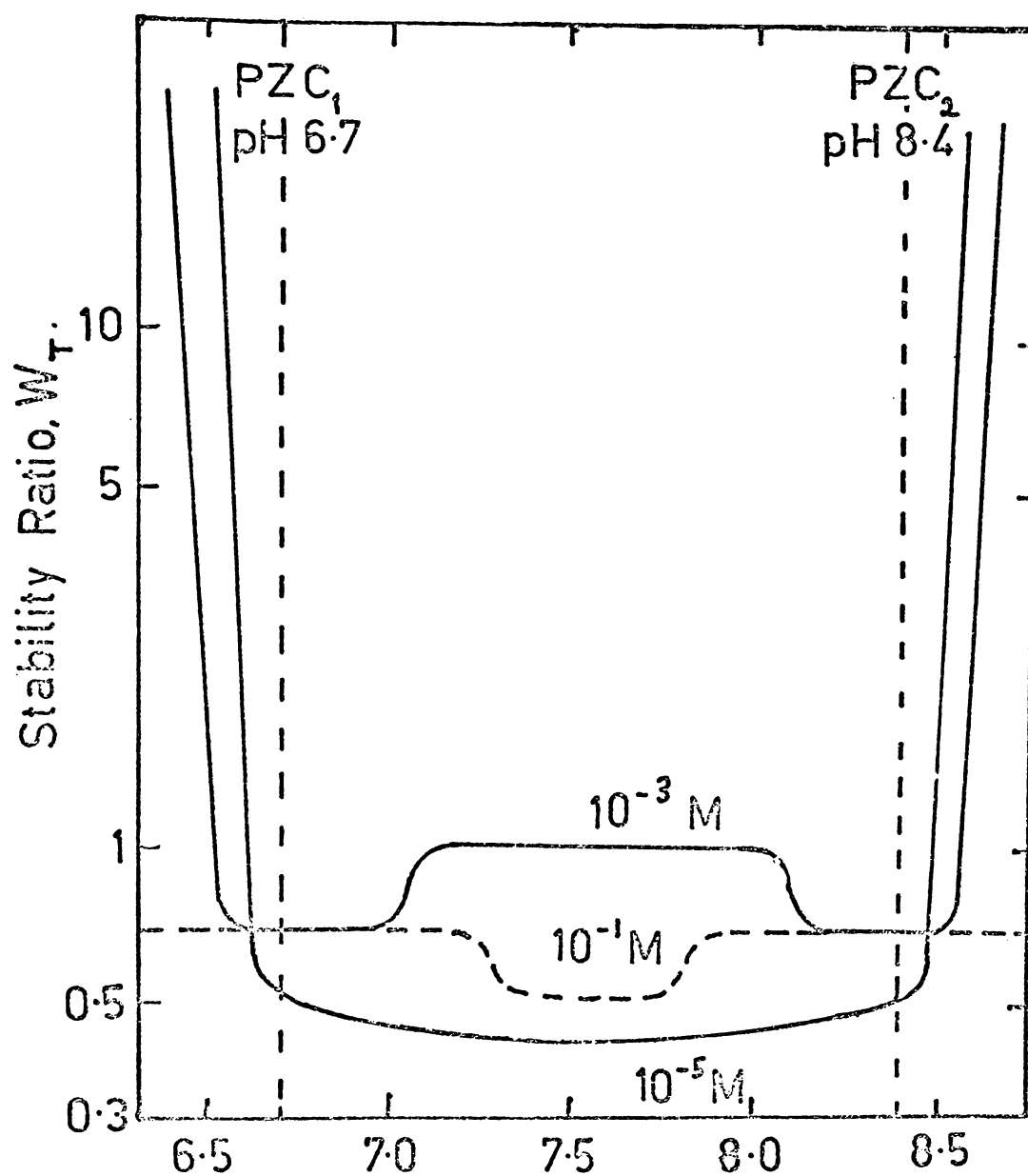


Figure 10.3. The variation of the stability ratio, W_T , with pH for equal numbers of two dissimilar particles as a function of total ionic strength of the system. (Redrawn from ref. 308.)

at plate edges in neutral and weakly acid environments permits interaction with the negative basal plane of adjacent particles and results in the formation of "edge-to-face" flocs with an open "cardhouse" structure.^{254,310} Addition of electrolyte may initially result in sol stabilisation because double layer compression reduces the overlap of the attractive double layers; large additions induce coagulation in a face-to-face manner.³¹⁰ The influence of cation nature parallels that for other negative hydrophobic sols with capacity to adsorb in a Stern layer; the stability decreases with increasing ion charge, ion radius and ease of hydrolysis.^{81,127,311} The rôle of aluminium, a matrix component, is very important; at low concentration it is capable of aiding flocculation dramatically. A large part of the enhancement observed with cations of high radius such as caesium is the result of displacement of aluminium from the matrix. Sodium is much less effective in this manner.³¹¹

The variation of the c.c.c.'s for the same salt with pH are quite similar to the electrophoretic mobilities and cation adsorption capacities of the same clays. For montmorillonite these are roughly constant in the pH region 4 to 7 with a change from 7 to 9 as edge sites are neutralised or deprotonated.^{136,140,311} For kaolinite there is a slow, but continuous, increase with pH.^{136,311} Coagulation with hydrolysable cations such as cobalt(II) and aluminium shows that the pH effect upon the ion controls the process to a much greater extent than the substrate.³¹¹ In water treatment processes using aluminium and iron(III) hydroxides removal of clay has been found to be most efficient at pH just below the metal hydroxide PZC.³¹²

Polyelectrolytes are quite variable in their effects upon clay sol stability. At low concentrations of polycations, low and moderate concentrations of polyanions and moderate amounts of non-ionic polymers sols of montmorillonite have been stabilised either by charge

effects or by particle separation; at higher concentrations the ionic polymers may cause flocculation by bridging.¹²⁷ Salt effects were found to be very important in flocculation of kaolinite by lignosulphonate.³¹³ Although sol stability was destroyed with the addition of this polyelectrolyte, it was regained when sodium chloride was added, possibly by weakening of polymer bridges. At higher salt concentrations flocculation proceeded by charge screening. The total system was not found to be amenable to complete interpretation by current stability concepts.

The flocculation of other clay minerals has not been as widely studied probably because they are not important industrial substances. The flocculation of halloysite was not unlike that of kaolinite and was in accord with its negative charge; the Schulze-Hardy rule was followed for the cations Na^+ , Ca^{2+} and Al^{3+} even though the latter is a matrix component and would be hydrolysed to some extent at the pH at which the determinations were made.³¹⁴

Aomine and Egashira¹⁴⁰ found for suspensions of some allophane clays in the pH region 4.5 to 6.5 (typical soil pH's) the concentrations of indifferent electrolyte required for the onset of flocculation decreased with increasing pH yet for montmorillonite they were constant. The concentration of divalent anion required was about one hundredth that of a monovalent anion; the comparable concentrations of divalent cation were equivalent to or more than those for monovalent cations. Furthermore the variations between equivalent cations (the orders of effectiveness were: $\text{Na}^+ > \text{K}^+ \sim \text{NH}_4^+$, $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Ba}^{2+}$) was the reverse of the lyotropic series. Horikawa and Hirose³¹⁴ discovered that the dispersions of allophane and also imogolite were both much more sensitive to anions than to cations. All these findings were taken to indicate the colloid was positively charged. The cation order observed will arise from the

adsorption preference of the positive surface; larger higher charged cations have been shown to adsorb more strongly (see Chapters Six and Eight). The nett surface charge will be increased and so greater concentrations of anions will be needed in the diffuse layer to effectively screen the repulsive Coulombic forces. This explanation is somewhat clearer than that of Aomine and Egashira, themselves.¹⁴⁰

10.5 Experimental Study

10.5.1 Introduction

Removal of colloids from suspension is generally most efficient if the conditions are such that rapid aggregation of the particles can occur. With aqueous clay suspensions these conditions depend upon the pH and nature and concentration of dissolved salts. The aim of this part of the experimental study was to find the optimum pH for flocculation of the Ohaupo allophane and the influence of the valence and concentration of some simple ionic species upon this process. The parameter used to determine the effectiveness of flocculation was the amount remaining in suspension 30 minutes after cessation of agitation (the method of residual turbidity). This method was chosen for two reasons: first, effective removal of the clay is desired if it is to be used as a flocculant; secondly, it was found that there was no immediate change in the optical density of any suspension upon cessation of agitation and so determination of the rate parameters would not have been straightforward.

The sol concentration chosen was such that at maximum flocculation the clay sedimented as a single body and left an almost clear, clay-free supernatant liquid; lesser concentrations tended to leave small flocs behind which settled out much more slowly. Finally, to obtain suspensions at various pH's but low salt concentrations, it was necessary to disperse the clay in solutions of different acidity and

then wash these by centrifugation with twice-distilled water.

10.5.2 Materials and Methods

Samples from a single clay preparation in the form of a suspension at pH 9.0 were acidified to various degrees with dilute hydrochloric acid, stirred overnight and then washed by centrifugation until the concentration of sodium in the supernatant was less than 10^{-5} M. At this point the centrifugate was resuspended in twice-distilled water and 10 ml aliquots taken in glass tubes to which were added suitable aliquots of solutions of the various salts. The final clay concentration was 13 g l^{-1} . The tubes were then sealed with plastic film (Gladwrap) and shaken vigorously; during the course of the following hour they were shaken again several times. After one hour had elapsed from the initial mixing the tubes were given a further vigorous shaking and left to stand for 30 minutes whereupon a sample of the supernatant liquid was withdrawn from a depth of 1.5 cm. The absorbance of this sample was determined at 490 nm using a Unicam SP 1800 spectrophotometer and the clay concentration found by comparison with standard curves. The material in the tube was resuspended by shaking and its pH recorded. In some instances the pH of the supernatant alone was recorded as well as of the dispersion; there was no significant difference.

10.5.3 Results

The results of the flocculation experiments are shown in figures 10.4a to c, where the percentage of the clay which remained in suspension for various concentrations of added electrolyte has been plotted against the pH of the suspension prior to salt addition. The ordinate is logarithmic to allow differentiation at higher flocculation to be noticeable. The most rapid and efficient

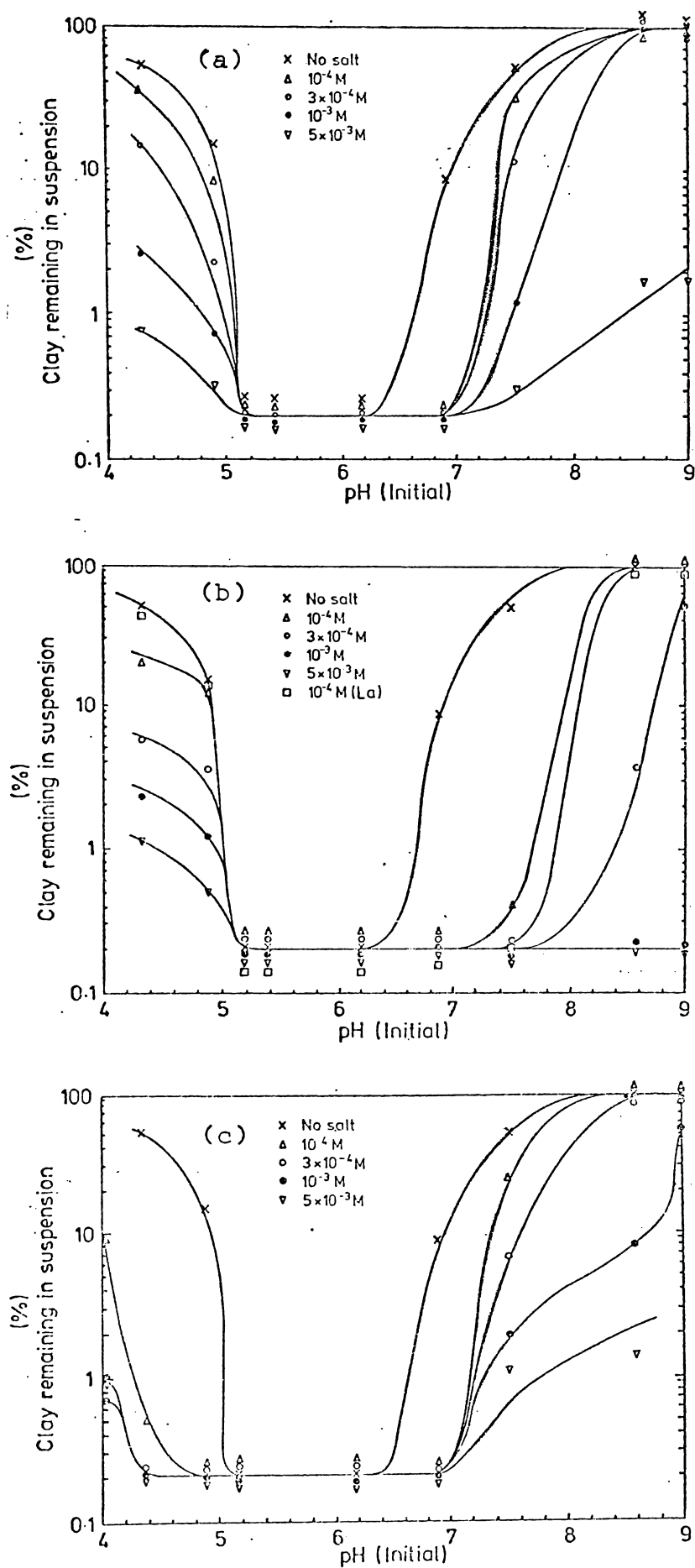


Figure 10.4. Flocculation of Ohaupo clay by (a) NaCl, (b) CaCl_2 (c) Na_2SO_4 .

flocculation was found to leave a residue of no more than 0.2% of the initial concentration of the clay present still suspended (the residual turbidity). Because of the fluctuations that occurred in this quantity all samples that had a residue of 0.2% or less were given the same value; i.e., 0.2%.

The flocculation by sodium chloride showed two points of note. First, the suspension was least stable near the clay IEP, i.e., near pH 6, the IEP from the electrophoretic determination (Chapter Nine). Secondly, an increase in the concentration of the electrolyte increased the pH range of sol instability in an approximately symmetrical manner about the IEP.

When the flocculation was studied in the sodium salt of a divalent anion, sulphate, the flocculation at pH's above the IEP was dependent upon the electrolyte concentration in a similar manner to its dependence upon the sodium chloride concentration. As the colloid was negatively charged its counterion would be Na^+ , the concentration of which would be twice that for the same molar strength NaCl solution and the increased flocculation can be associated with this alone. At pH's below the IEP the flocculation was greatly enhanced by the sulphate ion; at pH 4.4 the effect of 10^{-4} M sodium sulphate was similar to that of 5×10^{-3} M sodium chloride. The opposite effect was found with lanthanum and calcium chlorides. These multivalent cations were more active at higher pH than at low. Both were less effective at lower pH than sodium and lanthanum was actually not beneficial to flocculation in this region at all. At elevated pH calcium was a very effective flocculant (the added concentration of lanthanum was perhaps too low for the same influences to be seen from it). For a dispersion at pH 8.6 5×10^{-3} M sodium chloride and 3×10^{-4} M calcium chloride were about equally efficient as flocculants.

Upon mixing electrolyte and suspension the pH was generally found to change towards some pH value by an amount which increased with concentration and valence of the counterion. These pH's were 4.8 for sodium chloride, 5.9 for sodium sulphate and 4.3 for calcium chloride. For an indifferent salt this pH should be the PZC which was found to be near or a little below pH 5 (Chapter Five). The effect this change had upon the efficiency of flocculation is shown in figures 10.5a to c, where the amount which remained in suspension is plotted against the pH determined immediately after the withdrawal of the supernatant for turbidity measurement.

Below pH 5.5 there was little pH change with addition of sodium chloride but above pH 6 it is remarkable that the effective pH for flocculation was reduced and the range for rapid efficient flocculation was not much greater than in the absence of the salt. The flocculation with sodium sulphate was quite similar; the flocculation at higher pH was also due mostly to pH reduction and to a lesser extent to the electrolyte concentration. At lower pH sulphate effectively raised the pH into the fast flocculating range. With calcium pH reduction was important at high pH but at low pH the electrolyte concentration was the active force and to some extent the decreased pH encountered following interaction.

Finally, in figure 10.6, the flocculation of a suspension of the Mangawara halloysite in 10^{-3} M sodium chloride is depicted in the same terms as previously. Again at pH near the IEP, pH 3, flocculation was facile but as the pH was increased it became less favourable and at pH 8 the suspension was quite stable. This is again in concord with its electrophoretic properties.

10.5.4 Discussion

The first representation of the experimental data given allows a

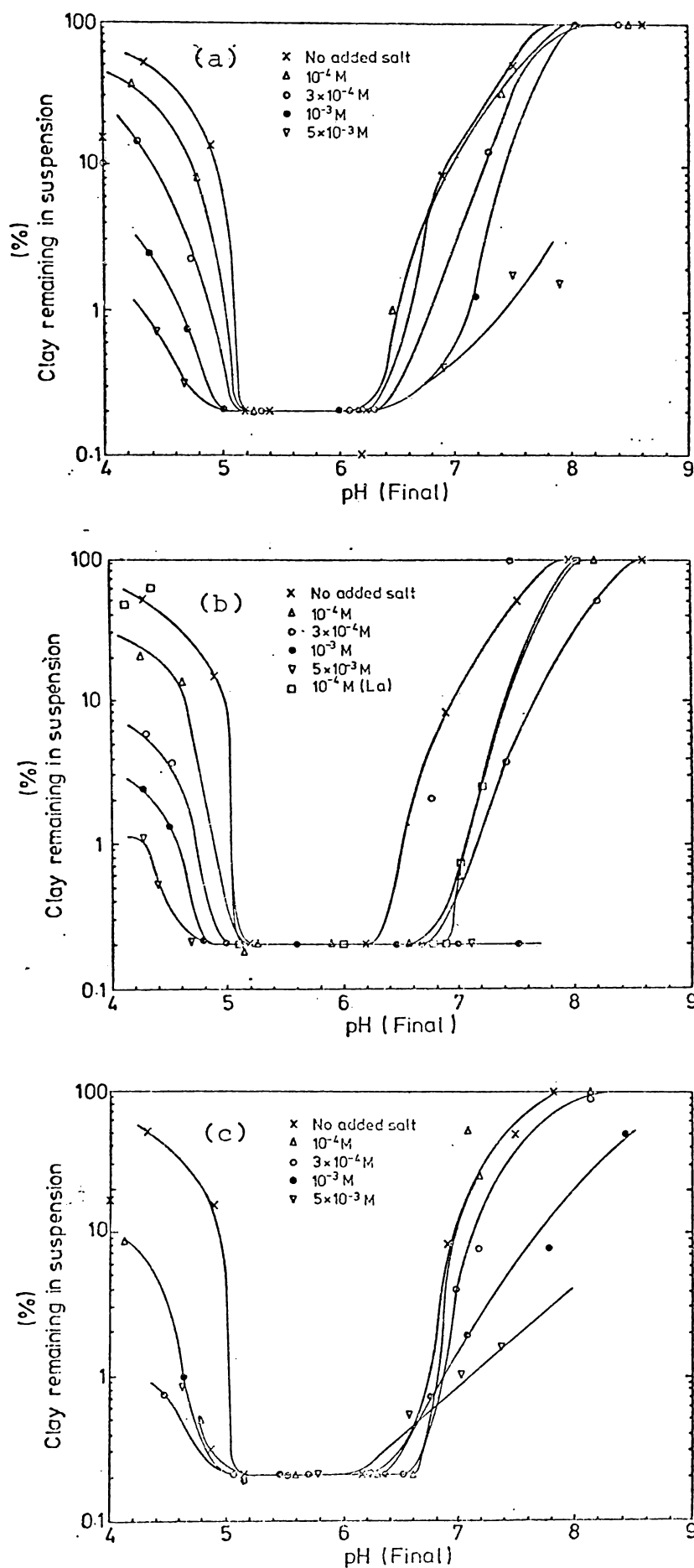


Figure 10.5. Flocculation of Ohaupo clay by (a) NaCl, (b) CaCl_2 , (c) Na_2SO_4 .

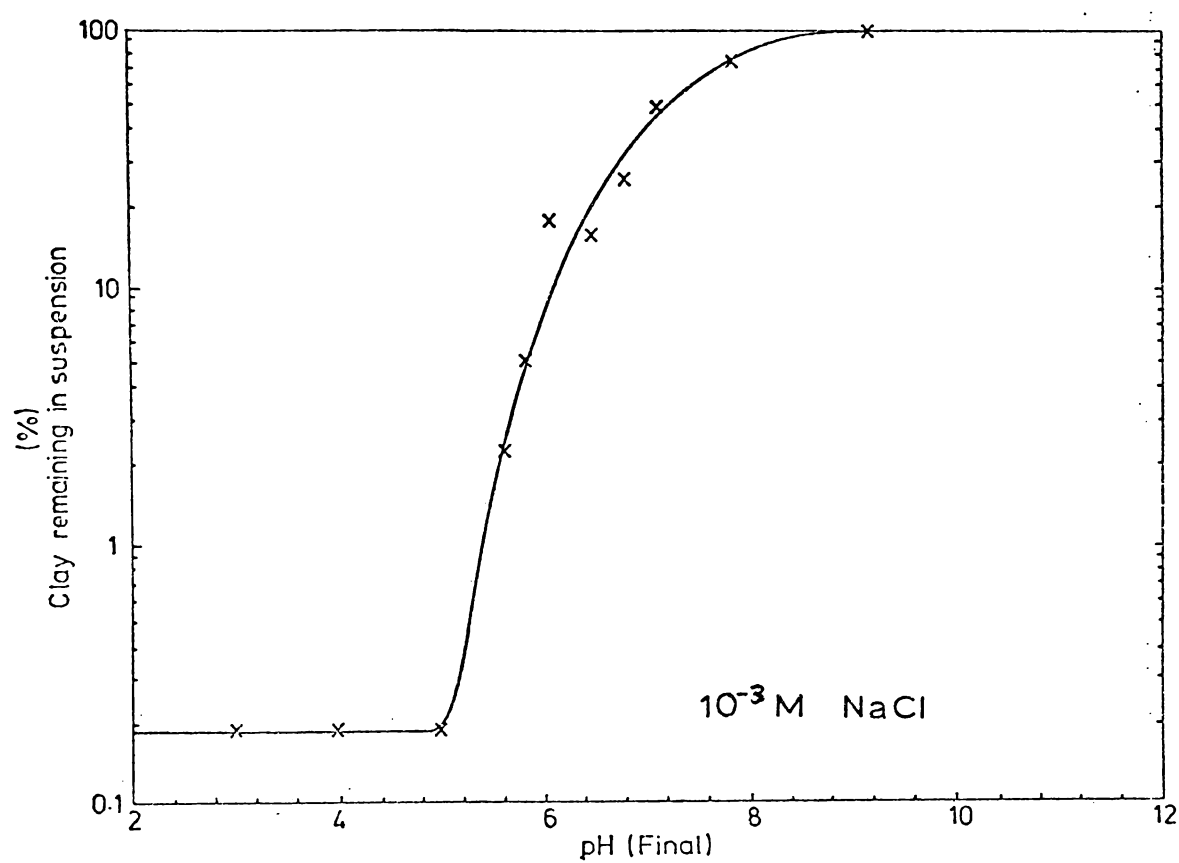


Figure 10.6. Flocculation of a Suspension of Mangawara clay as a function of pH.

consideration of the amount of electrolyte necessary to flocculate a suspension rapidly to be made. The second, where the pH of the actual process was plotted instead of the pH of the initial suspension, is more useful for general discussion of the various effects.

The flocculation of suspensions of allophane was found to be slower away from the IEP and unless there was more than 50% of the sol remaining in the dispersed state after 30 minutes standing subsequent to agitation it was generally found that it had all settled out overnight. Thus the amount remaining in suspension would be a measure of the reaction rate or the stability ratio, W . As stability increases so too does W . From the results obtained here it is not possible to correlate any actual percentage with a value of W except at maximum stability when W has no real value anyway. The plot of the residual turbidity against pH after a short period should be similar to plots of W against pH; in particular they would both have a minimum at the IEP and increase symmetrically with pH on either side of this point. This requirement is met for the plot of pH against percent remaining in suspension for the sodium chloride system, figure 10.5a at least. This plot shows that the flocculation of allophane suspensions have strong similarities with those of amphoteric hydrous oxides such as rutile and alumina.³¹⁵

The change in pH with electrolyte addition indicates that adsorption of cations or anions from the solution is releasing H^+ or OH^- respectively. These will contribute in part to the destabilisation as the pH changes in the direction of the apparent PZC for the particular salt. Generally this also means a movement towards the IEP resulting in a reduced surface charge and less effective surface potential. The strength of counterion adsorption which determines the release of p.d. ions, and hence pH determining ions, will be an important factor. Adsorption of calcium at lower pH, here less than pH 5, which is still strong (see section 8.3) will

enhance the positive charge in this region. Although calcium chloride solutions are twice as concentrated with respect to chloride ions they were found to be less efficient as flocculants than sodium chloride because of the extra charge neutralisation necessary. The flocculation of the initially stable suspensions to which calcium chloride had been added at higher pH only proceeded when there were significant quantities of the cation in solution. This can be seen from section 8.3 for the adsorption of both strontium and calcium whose adsorptions were relatively similar; if the added concentrations of these was 10^{-4} M it was nearly all adsorbed above pH 7, the pH above which the suspensions in the same concentration were not flocculating rapidly. Total adsorption of strontium from 10^{-3} M solution was not observed in the pH range studied and in fact at pH 8.3 only 50% of this cation had been adsorbed. Under these latter conditions, but with calcium as the cation, suspensions of allophane were found to flocculate rapidly. The partially destabilised sols in the calcium systems had not had sufficient calcium added to them to saturate their surface and also provide sufficient counterions to cause diffuse layer contraction as well. Neither was the amount enough to release sufficient H^{+} to reduce the pH to a region of rapid flocculation.

Sodium is less effective because it lacks the ability to adsorb as strongly and even when it is present in saturating concentrations it is much less efficient as a diffuse layer counterion.

Because of the influence of adsorption the addition of small quantities of highly charged ions may not have great effects upon the stability of allophanic clay suspensions; certainly not as great as is found with suspensions of PVC latex, silver chloride and other similar materials.²⁸¹

10.6.3 Conclusions

It has been found that stable suspensions of allophane can be coagulated by electrolyte by any of three mechanisms:

- (i) neutralisation of the effective surface charge by adsorption of its counterion,
- (ii) reduction of the effective surface charge by adsorption of potential determining ions released by the adsorption of surface charge counterions,
- (iii) screening of the effective surface potential by reduction of the double layer thickness following an increase in the electrolyte concentration.

These mechanisms may all occur separately or in unison. The efficiency of any electrolyte was found to increase with the valence of the surface charge counterion.

Coagulation of suspensions of allophanic clays could also be brought about by adding either acid or base to alter the pH towards their IEP's, the pH at which suspensions are most unstable.

As the IEP's of allophanic clays are usually near pH 6 they will be readily coagulated in waters near this pH provided their surface charge characteristics are not greatly perturbed by the adsorption of other materials.

CHAPTER ELEVEN

THE ADSORPTION OF ORGANIC SUBSTANCES BY ALLOPHANE

(I) PROTEIN

11.1 Introduction

The study of the complexes formed between clays and polymeric organic compounds has been of interest because of their importance both in nature and in industry. In soils and sediments organic matter from the decay of plants and animals becomes bound to the clay fraction. This process may protect the organic matter from further degradation; it may also assist binding of adjacent soil particles and influence soil structure. Clay-organic complexes are also important in such industries as wine making, paper production, and pharmaceutical and cosmetic manufacture.

Natural waters and effluents usually contain complex mixtures of dissolved organic substances. This has made it difficult to understand the factors that influence adsorption. For simplicity components of such mixtures may be interacted with clays or other solids. Often these components are themselves complex and so well defined systems containing "pure" clay minerals and simple organic compounds have been favoured by earlier workers for their investigations. Reviews of the preparation and properties of predominantly simple clay mineral/organic complexes have been prepared by Greenland,³¹⁶ Mortland,³¹⁷ Swartzen-Allen and Matijević,¹²⁷ Theng^{318,319} and Goring and Hamaker.³²⁰ This latter review deals in particular with synthetic organic chemicals.

11.2 Clay-Organic Interactions

A wide range of functional groups are found in natural organic compounds. Adsorption interactions between simple aliphatic compounds bearing these groups and clays have been studied. Generally the group dictates the mechanism of adsorption from aqueous solution. When ionisable groups are present the adsorption is similar to that of simple inorganic ions; anionic substances are not favoured by the surface at high pH but adsorb more intensely with acidification whilst cationic substances adsorb to a greater extent as the pH rises. These ions will compete with simple inorganic ions of the same charge. Because of the inherent negative charge of the layer silicate clays, such as montmorillonite and kaolinite, most studies have been made with organic cations rather than anions.

Neutral molecules with strongly polar groups like hydroxyl, e.g., alcohols, adsorb by ion-dipole interactions similar to the adsorption mechanism of water.^{127,317} Their adsorption is dependent upon the state of the surface; in particular the nature and surface concentration of the exchangeable cations as in some cases entry of the organic part into the coordination sphere of an adsorbed cation enhances adsorption.^{321,322} Hydrogen bonding from the organic molecule to the oxygen and hydroxyl groups of the clay is not very important because of its low strength when compared with ion-dipole forces if these are available. Van der Waal's forces are also operative but they are of consequence only for large molecules such as proteins and long chain polymers. With the layer silicates interlamellar penetration is sometimes an important adsorption process by which a much greater surface area becomes available for adsorption. Thus clay minerals able to expand, for instance montmorillonite, typically have greater capacities than those, like kaolinite, that do not.

11.3 Clay-Protein Interactions: A Review

The interactions of proteins with clays and similar materials have been studied for a variety of reasons. For instance, proteins are important components of soil organic matter, e.g., enzymes and the external surfaces of microorganisms. Furthermore milk proteins are used to bind kaolinite to paper to improve its texture and printing properties. The allophane-protein interaction has been investigated to determine the potential of this clay for use in the treatment of protein-rich effluents.¹¹ Some knowledge of the adsorption process has also proved useful in chromatography, an adsorption/desorption technique used for protein separation and purification.³²³

A large proportion of the studies of clay-protein interactions have been made using the expanding lattice mineral montmorillonite. It has been found that the amount of protein bound and the stability of the resulting complex are dependent upon a number of factors. The pH is known to have strong effects and maximum adsorption usually occurs near the isoelectric point (IEP) of the protein.³²⁴⁻³²⁶ The cation saturating the surface also has an important, if poorly defined, rôle.³²⁷ The cation characteristics that influence protein adsorption are valence, ionic radius, electronegativity and ionisation potential.³²⁸ The amount of protein bound by a montmorillonite was greatest when the clay was saturated with small cations of low charge. Saturation with large cations of higher charge reduced the capacity.³²⁸ Thus the readily exchangeable cations H^+ , Na^+ and Li^+ were all more effective at promoting protein adsorption than, for instance, Ca^{2+} or Al^{3+} .³²⁸ Increasing concentration of the electrolyte in the solution may influence the adsorption at both low concentration³²⁹ or at high.³²⁸ In the former case adsorption was enhanced; in the latter (above 0.5 M NaCl) it was reduced. The

adsorption mechanism was apparently at least partially cation exchange³²⁶ but because the electrolyte concentration had relatively small effects upon the extent of desorption, binding processes other than ion exchange or simple Coulombic forces would have also been effective.

Maximum adsorption of proteins has often occurred near the IEP of the protein with little regard to the nature of the surface. This behaviour has been observed not only at the clay mineral/aqueous interface but also at the stainless steel/aqueous³³⁰ and air/aqueous³³¹ interfaces. At the IEP the nett protein charge is zero, so that Coulombic forces with the surface will be minimised. In addition the protein solution is least stable with respect to precipitation. It has been pointed out by Mills and Creamer³²⁹ that in protein adsorption by clays the nature of the protein-solvent interactions must be of considerable consequence.

In some ways kaolinite- and halloysite-protein complexes are similar to those of montmorillonite; in particular the same charge characteristics of the protein are important. However montmorillonite adsorbs much more protein than either kaolinite or halloysite; often the amount bound is equal to its own weight whereas the other clays are 25 to 100 times less efficient.^{326,328,332} This quantity appears to be related to the surface area as determined by adsorbents which are capable of interlamellar penetration.

The rate of protein adsorption by porous materials has two parts. There is a fast reaction in the first few minutes when surface adsorption occurs. This is followed by a further loss of protein from solution at a slower and constant rate, dependent upon the molecular weight of the polymer, as it diffuses into the pores of the substrate where it becomes trapped and difficult to remove.³³³ Conformational changes, such as unfolding of adsorbed protein, may

not occur to any great extent,³³⁴ although this is still a point of controversy.^{335, 336}

It is apparent that all clay-protein combinations have their own individual properties which combined with the complexity of the protein structure make it difficult to fully understand the nature of their mutual adsorption complex.

11.4 Interactions of Allophane with Organic Substances

The available literature relating to the interaction of allophane with organic materials is sparse. In fact apart from biological organic matter there is but one report of any study of simple compounds. This was made by Theng³³⁷ who studied the adsorption of a variety of alkyl ammonium chlorides by allophane at constant pH. In the main these compounds were found to be physically adsorbed; a small part of the adsorption was by ion exchange. Theng suggested that the mode of interaction was a physical partitioning of the salt between the solution and the water of the interstices within the clay. The only other substances observed to be bound by allophane in this manner have been other simple salts at high concentration.^{30, 247}

In some Japanese soils, derived from volcanic ash, which experienced widely differing climate, situation and vegetation, high humus contents were found suggesting such organic matter was protected from bacterial attack. The activity of enzymes active in humus degradation was reduced by the presence of allophane.^{31, 32} The enzymes were apparently bound to the clay at both anion and cation adsorption sites; montmorillonite and kaolinite only adsorbed them at cation adsorption sites and were less effective at reducing the activity. Allophane also protected starch from degradation by enzymes. This protective action may explain why allophanic soils frequently contain a high content of organic matter. This can be seen from the

dark colour of their topsoils.^{22,243,338} Again allophane is displaying characteristics like those of the hydrous oxides, the soil components considered to be the most active in clay-organic reactions.^{339,340}

The allophane-organic complexes found in some New Zealand soils have been difficult to destroy using hot dilute hydrogen peroxide.¹⁶ Complexes of this type may be stabilised by adsorption to surface-bound aluminium. It has been suggested that this may make enzyme attack difficult by changing the molecular conformation.³⁴¹ Iron(III) was considered to be able to act in a similar manner.³⁴² Strongly acidic materials, such as the humic extracts of rotting clover, have also been observed to bind strongly to allophane, even in relatively alkaline media.^{343,344} Not only were these substances bound in greater quantity than to montmorillonite or halloysite, but the complexes formed with allophane were more stable. The properties of these complexes and the nature of their formation reactions suggests strong bonding of the type Hingston *et al.*^{133,202,203} referred to as "specific". This probably involves incorporation of the anionic organic groups, such as the carboxyl functions, into the coordination sphere of the surface aluminium with loss of bound water or hydroxyl groups. The binding would be similar to that of simple multivalent anions (see sections 6.3.5 and 6.4.5).

The adsorption of several animal proteins by allophane was found to be slow.¹¹ It continued for some hours and the amount adsorbed increased with concentration in a manner that suggested a maximum surface concentration. Near the protein IEP adsorption was enhanced, but at high protein concentrations the removal from solution may have been by surface precipitation rather than by adsorption as proteins are least soluble at this point. Suspensions of about 4 g l⁻¹ of allophane in 1 g l⁻¹ aqueous/protein solution were

able to adsorb up to about 100 mg g^{-1} ; i.e., about 10% by weight. (In similar circumstances halloysite adsorbed about 4 mg g^{-1} whilst montmorillonite bound about its own weight.^{326,332})

In this thesis the adsorption of the proteins, gelatine and bovine haemoglobin by Ohaupo allophane was investigated. Unlike the allophanes used by Milestone,¹¹ which had been freeze-dried, the Ohaupo clay was at all times maintained in an aqueous environment.

11.5 Adsorption of Proteins by Allophane; An Experimental Study

11.5.1 Materials and Methods

The proteins used were gelatine (ex Reidel de Haen AG) and haemoglobin extracted from beef blood (ex Sigma Chemical Corp.). Fresh solutions of these in distilled water were prepared when needed. Before use they were filtered through Millipore type GS ($< 0.22 \mu\text{m}$) filters; less than 2% by weight was not dissolved. Saturated mercury(II) chloride solution was added (one drop per 250 ml) to retard bacterial decomposition.

For adsorption experiments known aliquots of suspensions of Ohaupo allophane clay, previously equilibrated at differing pH by the addition of dilute sodium hydroxide or hydrochloric acid and then washed by centrifugation with distilled water, were added to suitable aliquots of the protein solution in glass vessels. These were closed and mixed on an end-over-end stirrer nominally rotating at 10 rpm but because it was connected to a simmerstat it operated for only 6 seconds per minute. Thus only one revolution was completed each minute. In this way mixing was maintained for several hours without coagulating the protein. Nevertheless at pH above 6 the haemoglobin tended to precipitate from all the solutions used especially if it was mixed for more than 3 to 4 hours. After 20 hours for the gelatine and $2\frac{1}{2}$ hours for the haemoglobin the pH of the mixtures were determined.

They were then centrifuged at 2500 rpm for 20 minutes in a MSE Multex centrifuge. The protein concentration in the supernatant liquid was measured. Gelatine was determined by preparing the purple complex formed with Biuret reagent (alkaline copper tartrate) following the method described in reference 345 (p. 1117). The optical density of the complex was determined at 550 nm with a Hilger Watts Uvispek spectrophotometer. Allowance for the turbidity of the suspension remaining after centrifugation at this wavelength was made by determining the optical density of the liquid without Biuret reagent and subtracting this from the value obtained for the complex. The true gelatine concentration was obtained by comparison with standard curves. Haemoglobin was determined by measurement of the optical density at 500 nm using a Unicam SP1800 spectrophotometer and comparison with standard curves. As the clay all flocculated in this series of experiments there was insufficient left in suspension after centrifugation to be of concern.

11.5.2 Results and Discussion

The adsorption of gelatine and haemoglobin onto Ohaupo allophane at various pH and concentrations is shown in figures 11.1 and 11.2. The two proteins displayed distinctly different adsorption behaviour. The adsorption of gelatine increased with both decreasing pH and increasing concentration whereas haemoglobin was adsorbed in greater quantity as the pH increased; a change in its concentration in the range studied had comparatively little influence as saturation was found for solutions of 100 mg protein for 1 g allophane. The behaviour was quite similar to that found with Tirau and Dunmore allophanes¹¹ with the adsorption increasing as the pH approached the IEP, 4.8 for gelatine and 6.8 for haemoglobin.³⁴⁶ The actual amounts adsorbed at pH 5 are compared in Table 9.1 with the relevant results

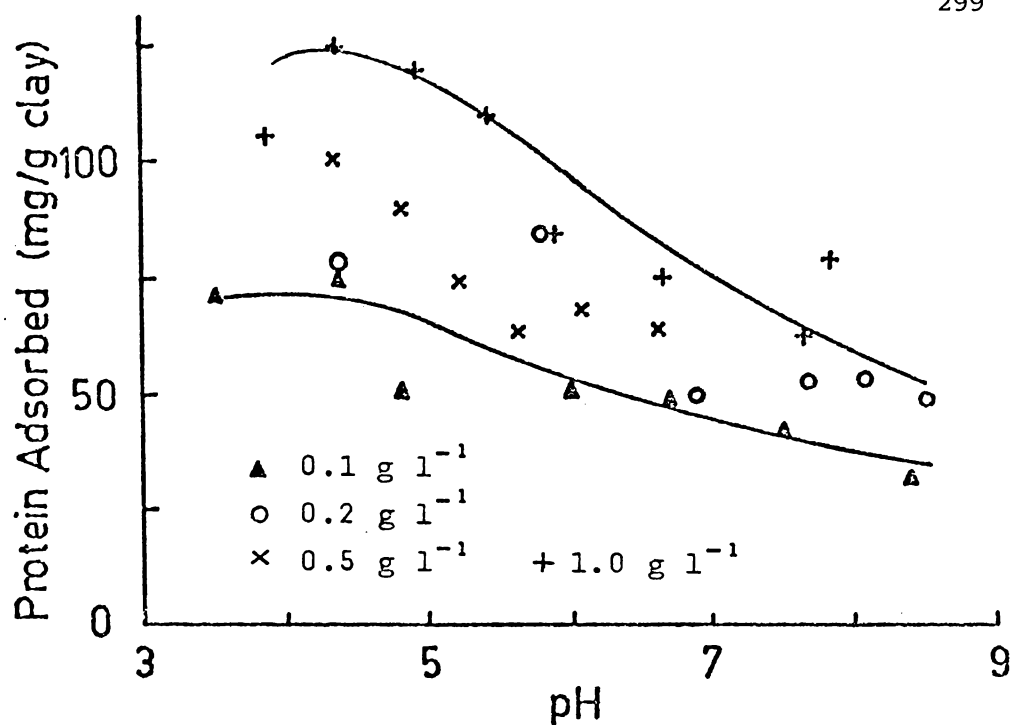


Figure 11.1. Adsorption of gelatine by allophane as a function of pH and protein concentration. Clay concentration 2.0 g/l.

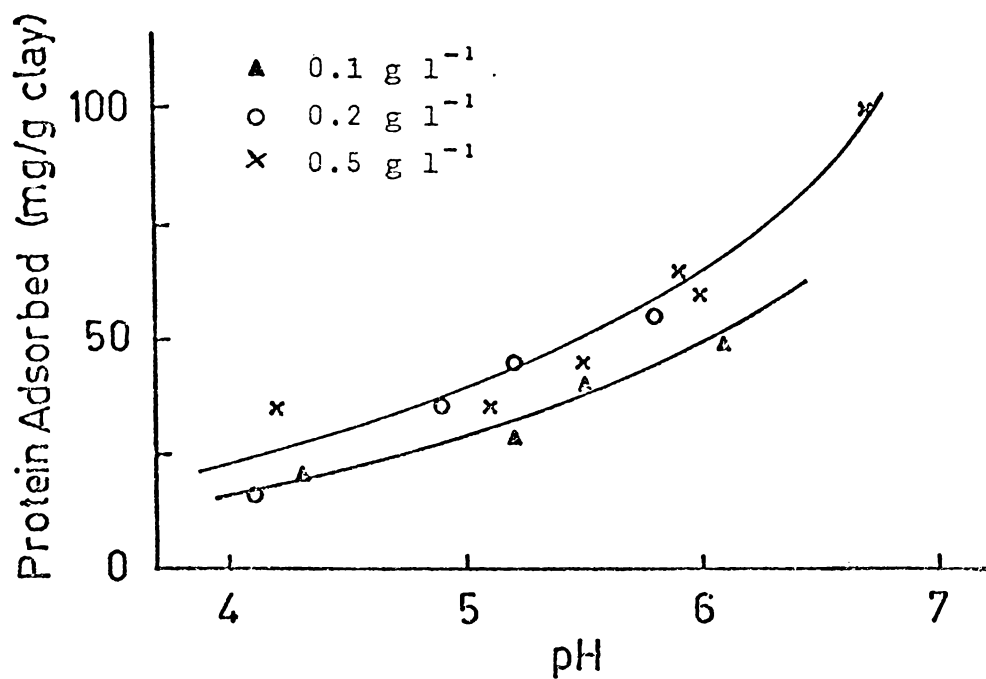


Figure 11.2. Adsorption of haemoglobin by allophane as a function of pH and protein concentration. Clay concentration 2.0 g/l.

Table 11.1 Adsorption of Gelatine and Haemoglobin by Various Allophane Suspensions at pH 5.

allophane	surface area $\text{m}^2 \text{g}^{-1}$	gelatine		haemoglobin	
		init.conc.	uptake	init.conc.	uptake
		(a) mg g^{-1}	(b) mg g^{-1}	(a) mg g^{-1}	(b) mg g^{-1}
Tirau ^c	350 ^{d,e}	150	40		
		92	37		
		65	27		
		48	8		
Dunmore ^c	569 ^{c,f}			180	35
				77	22
				36	17
Ohaupo ^d	420 ^{d,f}	200	80	100	35
	250 ^{d,e}	100	50	50	30

(a) initial relative concentrations of protein and clay; (b) weight of protein adsorbed per gram clay; (c) from reference 11; (d) this study; (e) surface area determined by adsorption of N_2 ; (f) surface area determined by adsorption of H_2O .

of Milestone.¹¹ The Ohaupo allophane appeared to have either a greater capacity to adsorb both proteins than the other two clays or alternatively it adsorbed them more readily. There are two major differences between the clays used here and those used by Milestone. At all times the Ohaupo clay was kept wet whereas the Tirau and Dunmore clays had been freeze-dried. The surface areas of the three clays also varied. A third possible cause of the differences may be in the morphology of the clays themselves.

The large surface area found for each clay by adsorption of water or nitrogen may not be closely related to the actual surface area available for protein adsorption. In Chapter Three it was seen that allophanes with large surface areas had much of this area associated with internal surfaces or pores. As allophane, being a three dimensional material, is unlikely to expand upon adsorption of substances causing lattice expansion, in montmorillonite for instance, all this internal surface area is not likely to be accessible to bulky protein molecules unable to penetrate narrow interstices. Furthermore such penetration would be a diffusion controlled process and would be slow.³³³ (This would explain the low rate of adsorption that occurred after the first rapid part (fig.11.3).) The Tirau allophane had not only a larger surface area than the Ohaupo clay; it also had a greater mean particle size and so a greater part of its surface would be associated with internal regions. For this reason it may not be able to adsorb as much protein.

Drying allophane is known to cause irreversible changes.²² One change may be to make more of the internal surface less accessible by collapsing interstices. Alternatively it may change the surface morphology. There is also a difference of note between the surfaces of the Tirau and Ohaupo clays (section 8.3.1). The first of these clays had aluminium in a state comparable to aluminium hydroxide and

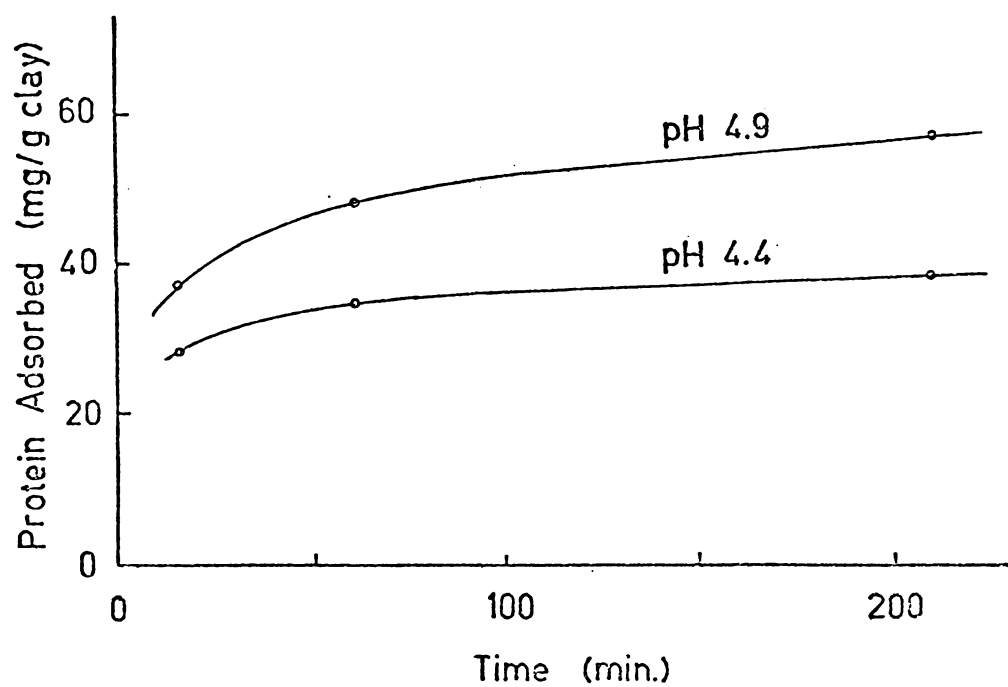


Figure 11.3. Variation of the adsorption of haemoglobin by allophane as a function of time. Clay concentration, 2.0 g/l. Protein concentration 0.2 g/l.

below pH 6 its cation adsorption sites were occupied to a greater extent by aluminium. Clays saturated with this cation have been found to be less effective protein adsorbents than those saturated with sodium or acid.³²⁸ However without concurrent experimentation the reasons for the differences must remain speculative.

The surfaces of allophane and halloysite or kaolinite differ in that their points of zero charge are about 2 pH units apart (see Chapter Five) and their isoelectric points are about 3 pH units apart. If protein adsorption was highly dependent upon the surface charge it might be expected that differences in the pH dependence of the interactions of these clays would be evident. However, there are no significant differences in the trends seen here and those observed for the other clay minerals as discussed in section 11.3. This is also in agreement with the predictions of the aggregation of particles of different nature (heterocoagulation) that were discussed in section 10.3. In the interactions of two colloids of different nature and size the charge properties of the smaller colloid will have the most influence upon the tendency for aggregation to occur following collision.

11.6 Conclusion

An allophanic clay that had at no stage been dried after extraction from the soil adsorbed significant quantities of protein from aqueous solution. Up to 100 mg protein per gram clay was observed to be bound; allophane had a greater capacity than kaolinite but less than montmorillonite. The adsorption behaviour was in general, similar to that found with other common clay minerals, the amount adsorbed appeared to be dependent upon the nature of the clay but variations with pH were a property of the protein. In particular the maximum binding appeared to occur at the isoelectric

point of the protein with little regard to the nature of the surface. This is in agreement with heterocoagulation theory; the charge of the smaller colloid, the protein, dominating the electrostatic forces.

Although the interaction of protein with allophane does not appear to be greatly different from its interactions with other clay minerals the use of allophane as an adsorbent for protein would derive advantages from the other properties of allophane. These include the greater ease with which allophane may be flocculated from near neutral suspensions and its high capacity for anions.

11.7 Applications in Industrial Processes

It has now been demonstrated that allophane has a strong affinity for proteins. There are a number of situations where this property might be exploited.

Proteins are present in the effluent streams of many food processing plants. Typical of these are slaughterhouses which have daily effluent discharges of the order of 10^4 m^3 . These contain about 450 to 650 mg protein per litre or about 4.5 to 6.5 tons per 10^4 m^3 .^{347, 348} At current prices the value of this material as an animal foodstuff is about \$400 per ton.³⁴⁸ This protein is a potentially valuable by-product and should be recovered. Furthermore, legislative pressures are being brought to bear on industries discarding such wastes because of their ability to cause serious pollution.

Although slaughterhouse wastes can be treated efficiently by biological digestion procedures these seldom actually recover a useful by-product and may convert the organic matter present into less readily adsorbed forms. Acid coagulation has been successful at removing a high proportion of fats and low IEP proteins such as gelatine from effluents.³⁴⁷ However high IEP materials such as haemoglobin are not

recovered readily. Other processes such as ion exchange are also available for the treatment of protein-containing wastes but in the main these tend to be expensive and unreliable.

Utilization of an adsorption/flocculation step, at near neutral pH after the acid coagulation, with an amphoteric flocculant would result in the removal of materials with high IEP's, such as haemoglobin, and a proportion of the soluble material remaining from the acid coagulation step. Provided the flocculant was non-toxic after rendering or autoclaving the material obtained would be useful for stockfood preparation. It is suggested that allophanic clays could be used in this manner.

A further situation where allophane, or a similar material, may be used as a protein adsorbent is in the separation of lactose from skim milk. This separation is achieved by crystallisation of the lactose from aqueous solution. This causes concentration of the whey proteins in the mother liquor. Eventually the solution becomes too viscous for further crystallisation and the solution is discarded. It may be possible to separate the protein from the sugar by adsorption by allophane and so allow a greater recovery of the lactose.

Proteins also contribute to the turbidity of many products, e.g., wine and beer. Allophane may have advantages over the other materials used for the removal of this turbidity.

CHAPTER TWELVE

THE ADSORPTION OF ORGANIC SUBSTANCES BY ALLOPHANE

(II) RIBONUCLEIC ACID

12.1 Introduction

Nucleic acid-mineral complexes have been studied for a number of reasons. These acids are constituents of the soil organic matter and although only a small part of the total they form a significant part of the organic phosphorus fraction. Smaller but similar substances, the inositol phosphates, become resistant to microbiological degradation at least in part because they form insoluble complexes with clay minerals.^{349, 350} The survival of microbial nucleic acid in the soil may be the result of similar complex formation.³⁵¹ Separation and purification of nucleic acids has often been desired as these minerals are of great interest in biochemistry and genetics. A common separation technique is by chromatography on hydroxyapatite, an adsorption/desorption process.³⁵² Montmorillonite has been used for purification and stabilisation of viral nucleic acids,^{353, 354} enzymes that may degrade or inhibit the acid being adsorbed strongly and deactivated.³⁵⁵

12.2 Clay-Nucleic Acid Interactions

Nucleic acids are polymers of nucleotides which are molecular groups of three parts; a phosphate group, a pentose and a heterocyclic base or nucleoside. The polymer spine is formed by the sugars linked through the 3' and 5' positions by the phosphate and the base is condensed to the sugar by the aldehyde group. There are two forms of nucleic acid. In ribonucleic acids (RNA) the pentose is ribose and the bases are either of two substituted purines, adenine and guanine, or either of two pyrimidines, cytosine and uracil. Deoxyribonucleic acid (DNA) is similar but the sugar is deoxyribose and thymine is present but not uracil. The unique nature of each nucleic acid is determined by the order and number of the nucleosides in the polymer.

The combinations of materials that form a nucleic acid give it basic groups, acidic groups, (the phosphate) and neutral groups, (the sugar residues). All of these are capable of binding to charged surfaces and so, like many other biocolloids and polyelectrolytes, adsorption proceeds readily. Primarily as a result of the acidity of the phosphate part (pK_a about 0.7 to 1.0³⁵⁶) the total molecule is acidic, it has a low IEP and so it may be expected to behave like an anion at charged surfaces.

Like the proteins, nucleic acids adsorb to surfaces most strongly near their IEP (also their point of minimum solubility), i.e., at low pH. When the molecule is anionic it will still sorb to negative surfaces unless the surface potential exceeds a limiting value.³⁵⁷ For clays^{349,355,358} and hydrous oxides³⁵⁹ the pH becomes particularly important in determining the extent of the adsorption, so too is the electrolyte concentration as the presence of salt enhances adsorption.^{355,358}

DNA and RNA adsorption by montmorillonite in the region pH 5 to 9 was confined to the external surfaces and, like the surface charge, it

was constant,³⁵⁸ although it was enhanced by divalent cations. With decreasing pH the adsorption increased markedly and was accompanied by lattice expansion, i.e., it was also interlamellar. This mineral also had a very large capacity for RNA; at some undefined point when 24 mg RNA had been added per mg clay in the suspension the uptake was 16 mg mg⁻¹. However, alumina at pH 3.0 was saturated by the adsorption of only 0.75 mg g⁻¹.³⁵⁹

Upon adsorption of DNA by montmorillonite at pH $\leq$ 5.0 there was a ready lattice expansion to 1.9 nm and, with further DNA addition, this increased to 3.7 nm.³⁵⁸ As the DNA molecule has a diameter of about 2.0 nm the first expansion would correspond to a single layer of interlamellar nucleic acid and the next to a second. RNA also showed a similar lattice expansion to 1.8 and 3.6 nm respectively. Thus an adsorbed monolayer of RNA lying flat on a surface would be about 1.8 nm thick and completely cover 500 m²g⁻¹. However, loops and kinks in the polymer would make each molecule effectively cover a wider area. On this basis the amount of RNA adsorbed by a montmorillonite with an internal surface area of 382 m²g⁻¹ would be, if it was bound as a complete monolayer in the interlamellar region, somewhat less than 0.38 g g⁻¹. Greaves and Wilson³⁵⁸ found RNA uptake at pH 5.0 by such a clay was about 0.21 to 0.24 g g⁻¹, or a coverage of about 850 m²g⁻¹.

The importance of the surface charge properties has been illustrated by mica which sorbed DNA only when the potassium ions of the cleavage surface had been replaced by aluminium.³⁶⁰ The adsorption complex was said to involve a phosphate-aluminium linkage similar to that of the aluminium-sulphate complex described by Rankin and Wilson.³⁶¹ Subsequently studies of phosphate and sulphate adsorption by mica exchanged with iron(III) and aluminium has shown the anion adsorption was associated with adsorbed cationic hydrolysis

products.^{362, 363} The DNA adsorption was probably also associated with similar species rather than discrete trivalent cations.

The anionic nature of the nucleic acid molecule in neutral solutions is also evident from its chromatographic behaviour on hydroxyapatite (a form of calcium phosphate). Generally separations have been carried out in solutions of near neutral buffers³⁵⁶ so that the adsorption complex is not excessively stable. The nucleic acid can then be eluted by strong phosphate solutions, the inorganic phosphate replacing the polymer phosphate at the surface.

12.3 Adsorption of RNA by Allophane; An Experimental Study

12.3.1 Materials and Methods

Solutions of yeast RNA (ex BDH Ltd.) were prepared in distilled water. These were filtered through Millipore type GS filters and stored at 4°C to retard bacterial decomposition. Solutions were used within 12 hours of preparation. The clay suspensions for most experiments were prepared as for the protein adsorption studies (section 11.5.1). The homoionic clays were prepared by treating suspensions of allophane with 1 M solutions of the neutral chlorides of the desired cation twice, the second time overnight, and then washing by centrifugation with distilled water until the supernatant liquid was free of chloride (0.1 M silver nitrate).

For adsorption experiments suitable aliquots of RNA solution were added to known volumes of allophane suspension, and electrolytes if necessary, in plastic centrifuge tubes. These were closed with rubber bungs and agitated by end-over-end rotation. After the required time the pH was determined and the clay and clay-RNA complexes were separated from the liquid by centrifuging, first at 2,500 rpm for 10 minutes in a MSE Multex centrifuge and then at 20,000 rpm for 10 minutes in a Sorvall RC2-B refrigerated centrifuge

at 10°C. The optical densities (OD) of the aqueous phase were measured at 320 and 258.5 nm with a Cary 17 Spectrophotometer. Samples were diluted with distilled water if their OD exceeded 1.0; below this for RNA solutions the Beer-Lambert law held. The absorbance also varied with pH but within the range 3 to 9 the variation was less than 3% and so was not corrected for; outside this range the pH was returned towards neutrality by the addition of neutral phosphate buffer. In some cases clay residue tended to remain in suspension and this interfered in the determination of the acid concentration at 258.5 nm. In figure 12.1 the visible-u.v. spectra of a suspension of fine allophane (< 0.2 μm) and also a solution of RNA are shown. The acid solution did not absorb at 320 nm at all and so, as a 1.00 mg ml⁻¹ solution had an OD_{258.5} of 25.4 the following equation was used to obtain the acid concentration;

$$[\text{RNA}] = \frac{1}{25.4} (\text{OD}_{258.5} - 1.65 \text{OD}_{320}) \quad (12.1)$$

Adsorbed nucleic acid was taken as the difference between the amount initially present and that found to be remaining in solution.

For the desorption experiments an RNA-allophane complex was formed by suspending 250 mg of washed sodium-form allophane in 40 ml of 500 mg l⁻¹ RNA solution at pH 5.5 and stirring for several hours. The clay was gathered by centrifugation and resuspended in the same solution, stirred overnight, concentrated again by centrifugation and then washed three times at the centrifuge with distilled water. After resuspension in distilled water the complex was divided into six parts, the various reagents were added and then the samples were mixed for 24 hours by end-over-end rotation. After centrifugation as above the supernatant solutions were analysed for RNA.

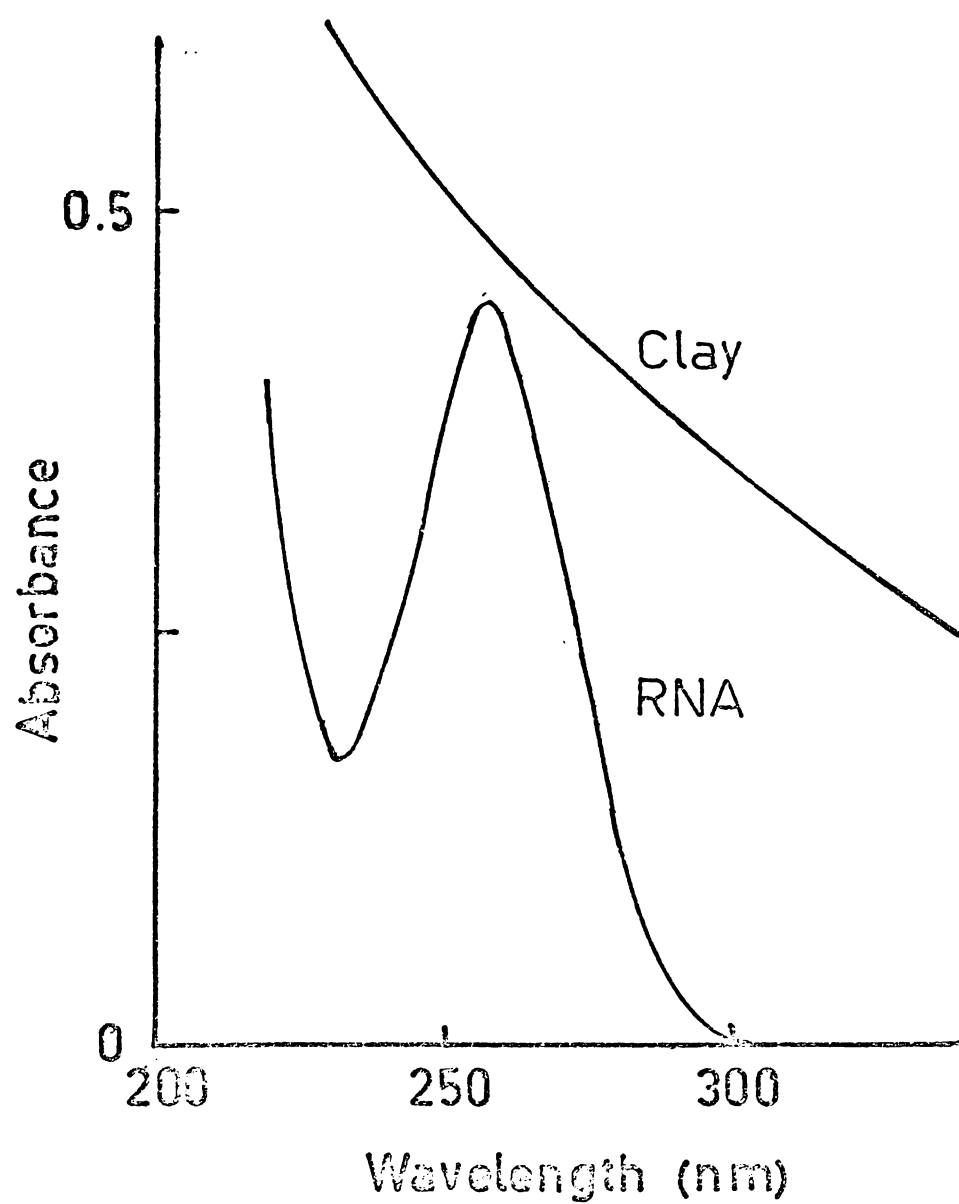


Figure 12.1. Absorbance spectra of yeast RNA and a suspension of Ohaupo allophane.

12.3.2 Results

The initial rate of adsorption from a neutral solution of RNA (45 mg l^{-1}) by Ohaupo allophane (2.9 g l^{-1}) was rapid. Within 30 minutes 85% of the maximum adsorption had occurred (fig. 12.2); 95% had occurred within 2 hours but adsorption did not appear to be complete until 12 hours had elapsed. For all subsequent experiments 24 hours were allowed for the reaction. This rate is slower than that reported for montmorillonite³⁵⁸ but the conditions at which that rate was observed were not reported.

The formation of RNA-allophane complexes was very dependent upon pH and proceeded more readily if the solutions were acidic (fig. 12.3). The actual amount adsorbed increased with electrolyte concentration over the whole pH range although the effect was more marked at higher pH.

The nature of the anion of the electrolyte, whether chloride, nitrate or sulphate made no difference to the adsorption from 10^{-2} M solutions (fig. 12.4). However there was a large difference in the influences of mono- and divalent cations. Figure 12.5 shows the adsorption of RNA onto allophane from 10^{-2} M solutions of sodium and calcium chloride. This effect was even more pronounced when observed at constant pH but with varying salt concentration. Figure 12.6 shows the change in adsorption from neutral solution with increasing concentration of the chloride of sodium, magnesium and calcium, whilst the effect for the two divalent cations at pH 8.5 to 9.5 is given in figure 12.7. (All solutions were at least $2 \times 10^{-4} \text{ M}$ in sodium because the RNA was obtained as the sodium salt.) There appears to be no significant difference between either cation. Both were able greatly to enhance the adsorption of RNA, being effective at one hundredth the concentration of sodium required for the same result.

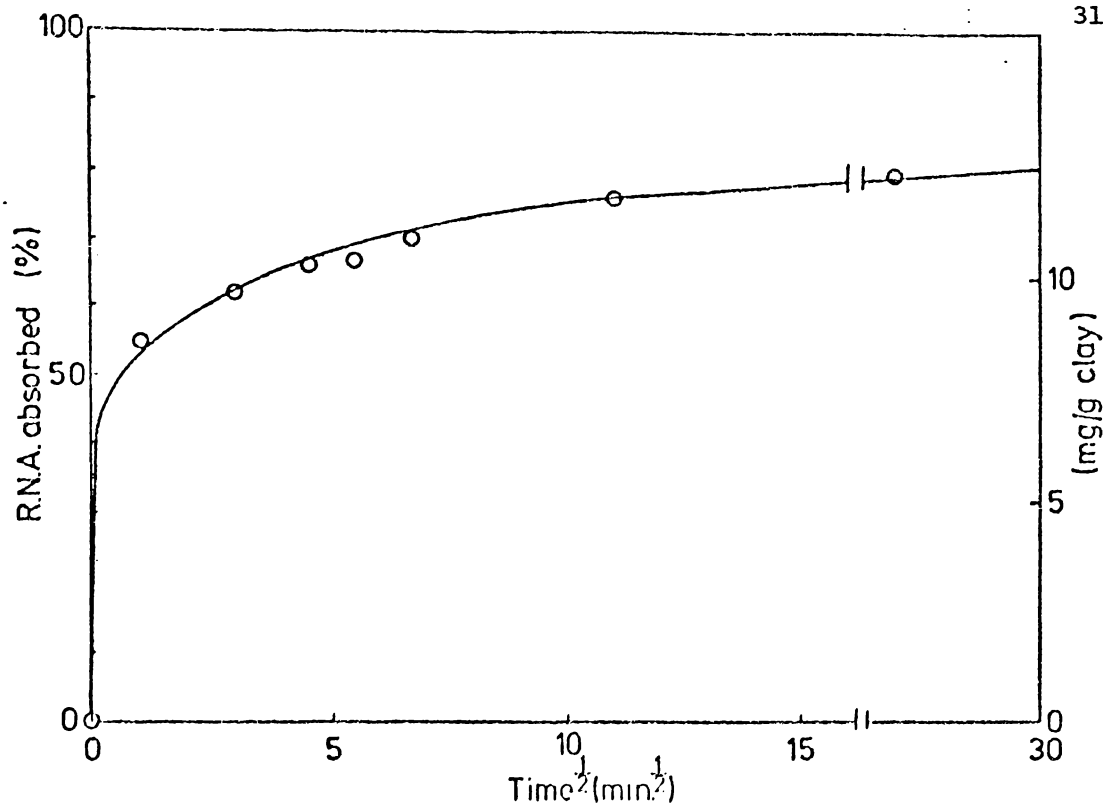


Figure 12.2. Adsorption of RNA by allophane as a function of time.

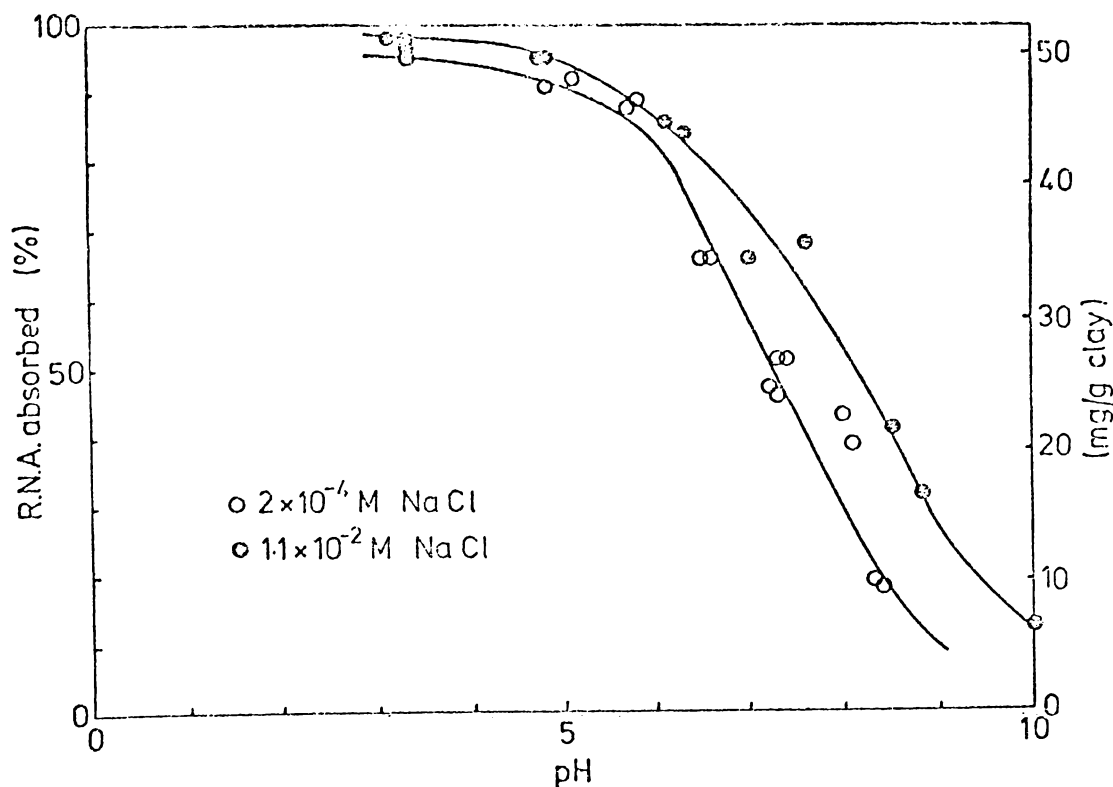


Figure 12.3. Adsorption of RNA by allophane as a function of pH and electrolyte concentration.

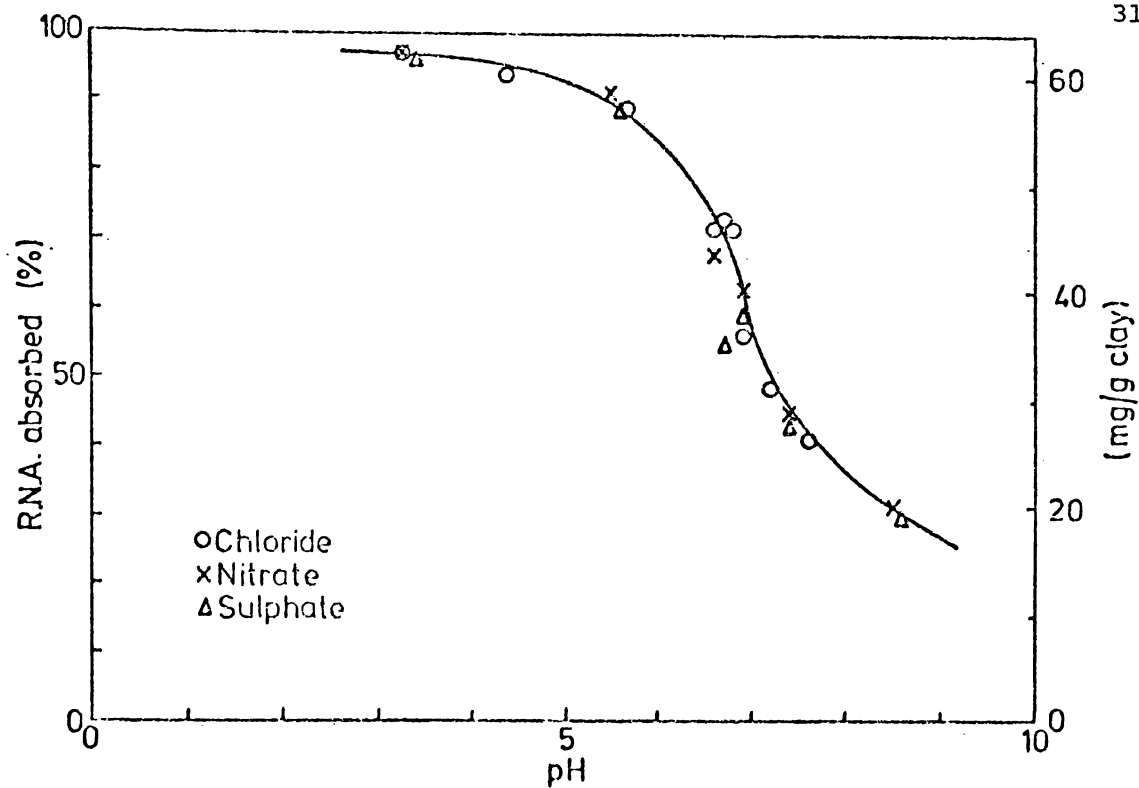


Figure 12.4. Adsorption of RNA by allophane as a function of pH and anion type.

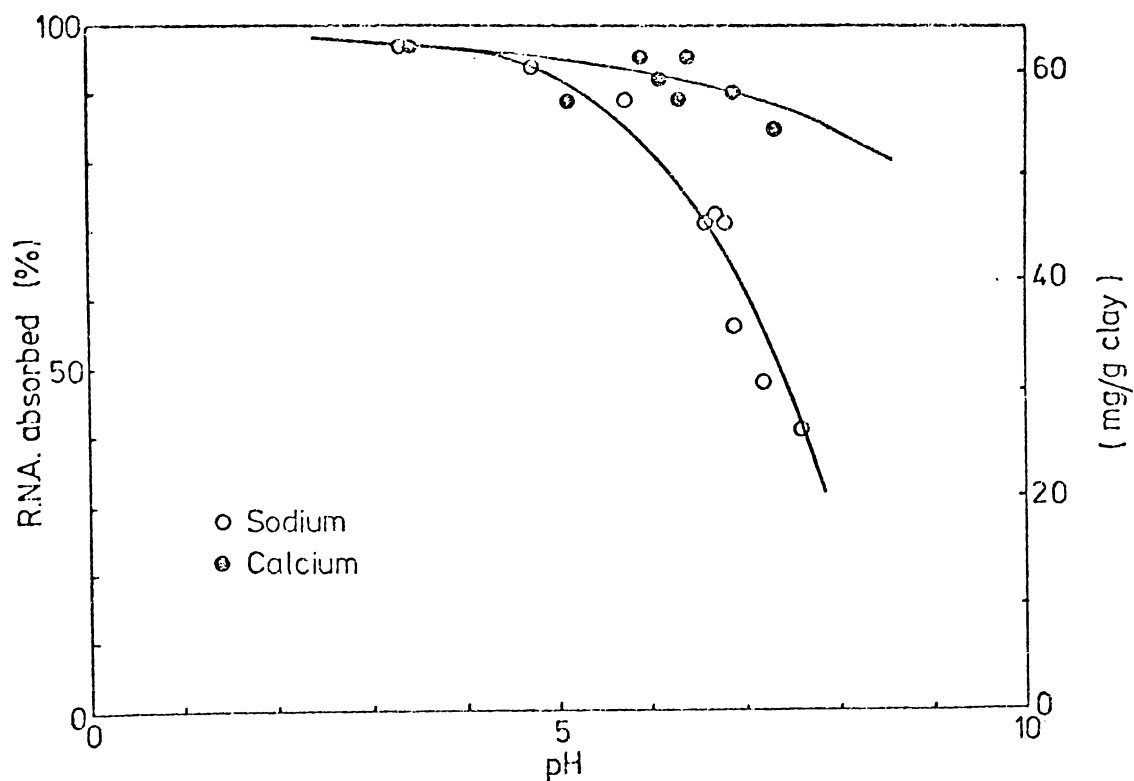


Figure 12.5. Adsorption of RNA by allophane as a function of pH and cation type.

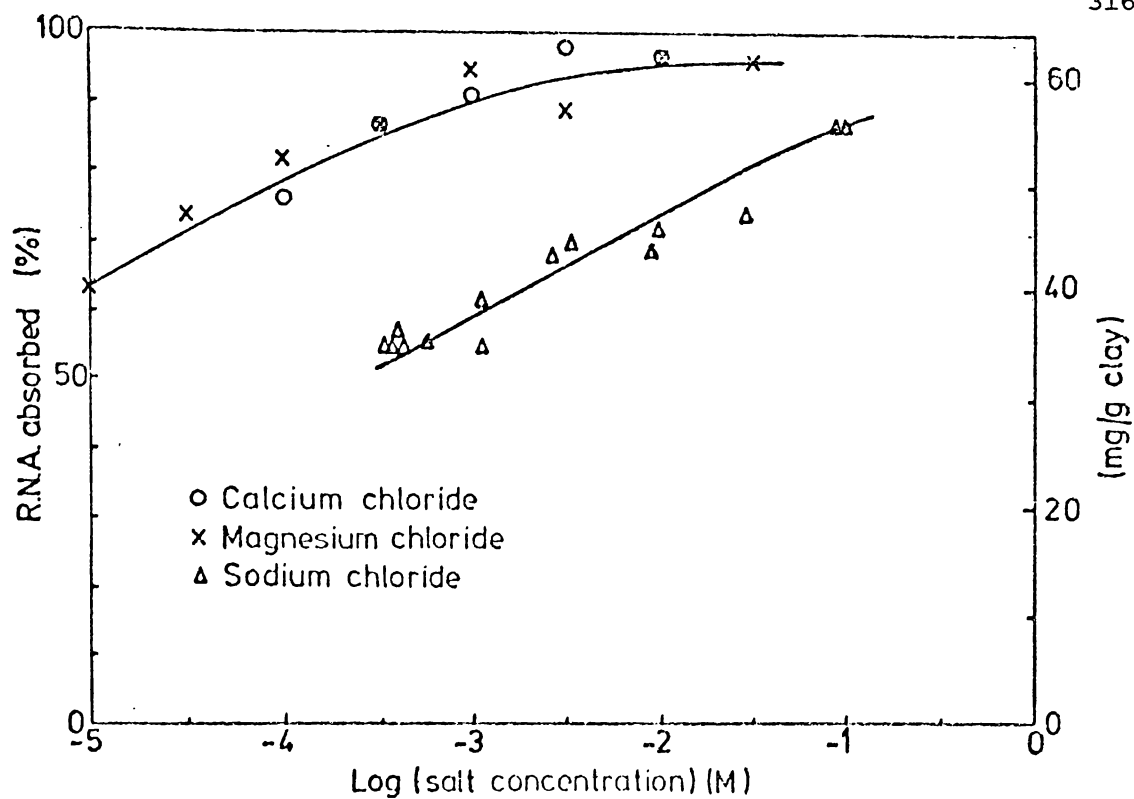


Figure 12.6. Adsorption of RNA by allophane as a function of electrolyte nature and concentration.

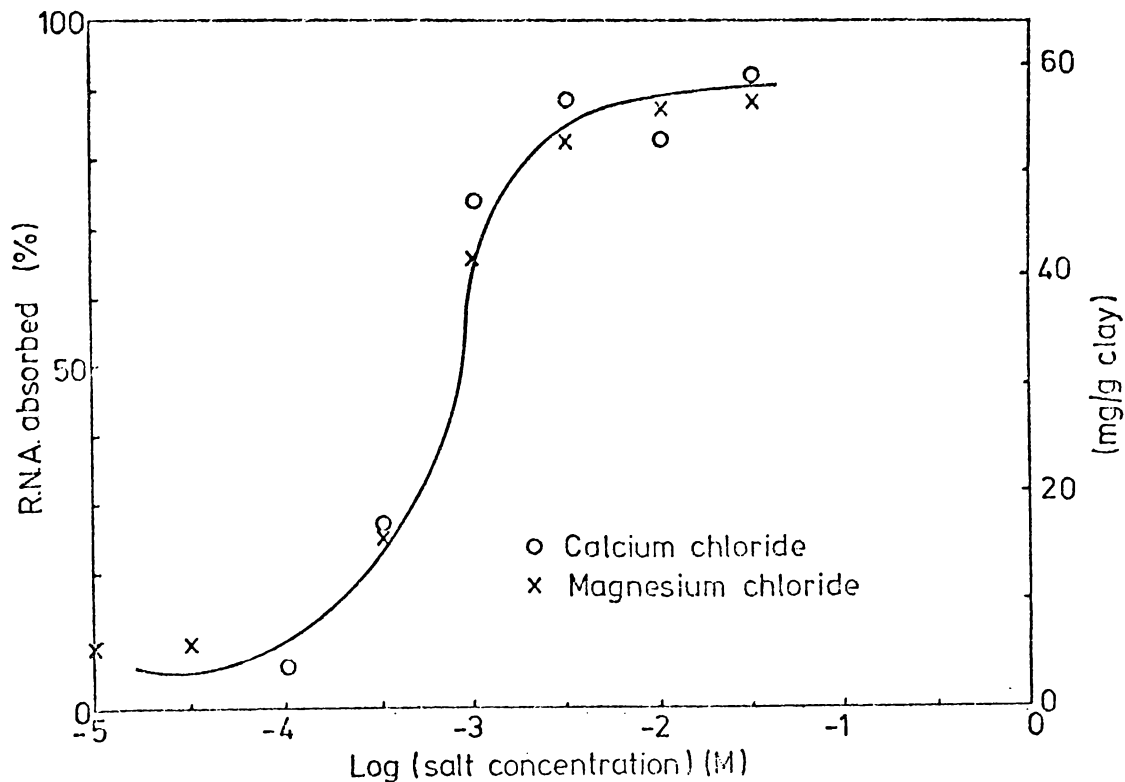


Figure 12.7. Adsorption of RNA by allophane as a function of the concentration of the chlorides of magnesium or calcium.

The strong adsorption induced by the divalent cations was also apparent when they were already present upon the mineral surface. The results for RNA adsorption onto various homoionic forms of Ohaupo allophane are shown in Table 12.1. Again calcium and magnesium were similar in their influences; the adsorption by clays bearing these two cations was much greater than onto the sodium form.

Table 12.1 Adsorption of RNA by Homoionic Forms of Ohaupo Allophane
(Initial concentrations: clay, 4.55 g l^{-1} ; RNA, 150 mg l^{-1})

Saturating cation	pH	RNA adsorbed (mg g^{-1})
sodium	7.5	8.1
magnesium	7.2	29
calcium	7.0	31

The effect of increasing the nucleic acid concentration at low electrolyte concentration and constant pH and clay content is shown in figure 12.8. The high adsorption from low concentration is typical of polyelectrolyte adsorption. The maximum amount of RNA adsorbed was 33 mg g^{-1} . Also shown in this figure are the amounts of calf thymus DNA and yeast RNA adsorbed onto alumina (from ref. 359). Even though the adsorption onto alumina was carried out from a more concentrated salt solution ($5 \times 10^{-2} \text{ M}$) allophane was much more effective as an adsorbent. Both materials had less capacity than montmorillonite which adsorbed about 100 mg g^{-1} of RNA at the same pH.³⁵⁸

The data used for figure 12.8 is shown again in figure 12.9 where it has been plotted using the Langmuir equation (6.5). From the slope the monolayer coverage would be 38 mg g^{-1} . Based on a surface area of $250 \text{ m}^2 \text{ g}^{-1}$ for the clay this would be a coverage of $6,600 \text{ m}^2 \text{ g}^{-1}$

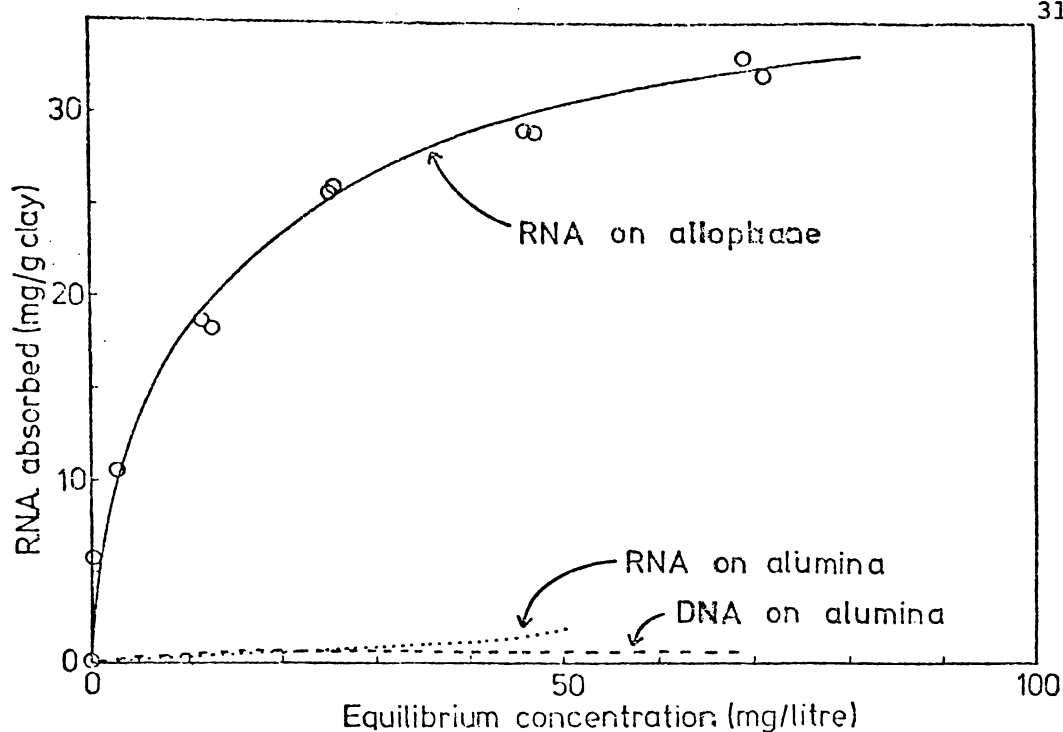


Figure 12.8. Adsorption of RNA by allophane at pH 6.0 as a function of RNA concentration. Clay concentration 4.55 g/l. Also, (from ref. 359) adsorption of RNA and DNA by alumina at pH 3.5. Alumina concentration 100 g/l.

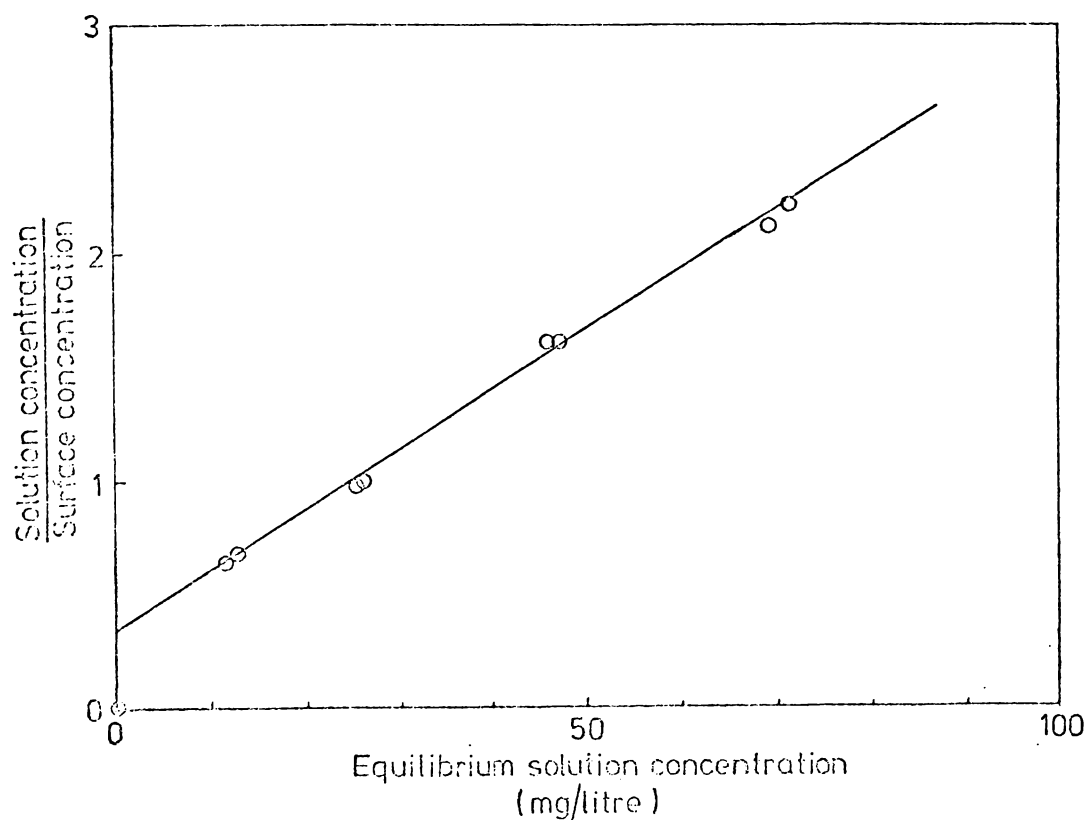


Figure 12.9. Adsorption of RNA by allophane: Langmuir representation of Figure 12.8.

by the acid or about eight times that on montmorillonite.

The amount of RNA desorbed from an adsorption complex with allophane by a number of reagents is detailed in Table 12.2. The most effective reagent was 0.5 M sodium carbonate which raised the pH to 12. Raising it to 9.0 with dilute sodium hydroxide also brought about a large amount of desorption but adding sodium hexametaphosphate at pH 5.5 had the same result. Although an increase in the concentration of indifferent electrolyte has been seen to cause an increase in adsorption, raising it to 5 M resulted in more RNA desorbing from the complex than in distilled water at the same pH. Acidification stabilised the adsorption complex.

Table 12.2 Desorption of RNA from Ohaupo Allophane by Various Reagents
(RNA-Clay complex composition: 29 mg RNA/g clay)

Reagent	pH	percent desorbed
Water	6.3	1.5
Hydrochloric acid (to pH 3.0)	3.0	0.4
Sodium chloride (5 M)	6.3	4.0
Sodium hexametaphosphate (1.2 g l ⁻¹)	5.5	22
Sodium hydroxide (to pH 9.0)	9.0	29
Sodium carbonate (0.5 M)	12	98

12.3.3 Discussion

The adsorption of yeast RNA by allophane showed a number of features characteristic of anions adsorbing at the aqueous/hydrous oxide interface. First, it increased with decreasing pH, i.e., as the

anion was hydrolysed and approached a neutral state and also as the surface became more positive and anion attractive. Secondly, it was not effected by the replacement of monovalent anions in the electrolyte by divalent anions. Thirdly, divalent cations enhanced adsorption beyond that found for an equivalent concentration of monovalent cations. Fourthly, RNA was desorbed by a pH increase or by the addition of strongly adsorbing, highly charged, small anions such as hexametaphosphate, both of which made the effective surface charge highly negative. This behaviour is very similar to that displayed by sulphate and phosphate at the allophane and synthetic aluminosilicate surface (see section 6.4.5). As the phosphate group is the anionic part of the RNA molecule, it must be the effective binding part; this would be readily associated with the allophane surface aluminium hydroxide.

The influence of the concentration of indifferent electrolyte upon the adsorption is similar to that upon heterocoagulation. If the salt concentration is increased the effective surface charge of the polymer is reduced by charge neutralisation and diffuse layer compression; this also causes its electrophoretic mobility to decrease.³⁶⁴ In this situation the polymer is approaching a low charge state similar to that at its IEP, the pH at which it is least stable in solution. Nett electrostatic repulsions are also reduced and so adsorption is enhanced. At very high electrolyte concentrations the surface will be saturated with the anion of the salt which could then displace the RNA phosphate from the surface to some extent. These effects are analogous to those observed not only for nucleic acids but also for proteins.

The surface area of allophane (BET N_2) occupied per unit weight of RNA was about 8 times the area occupied by a monolayer of the same amount of montmorillonite. The montmorillonite coverage assumed a

1.8 nm thick layer, i.e., the polymer lying along the surface so that multipoint adsorption could occur. As the coverage on allophane was even greater it is likely that RNA was also bound in a similar manner. The total amount adsorbed does not appear at first to give complete monolayer saturation. There may be two reasons for this. First, saturation may not need complete surface coverage; alternatively and more probably, all the surface may not be available to the nucleic acid. The second reason is more likely as much of the allophane surface is internal and associated with small pores and interstices. If these are less than 1.8 nm wide they will not be accessible to RNA while still being open to the small molecules used for surface area determination. Furthermore interstices of width between 1.8 and 3.6 nm will be able to adsorb only a single layer of RNA so that the apparent surface occupied by each molecule would be approximately doubled. As such small openings would make up a large part of the allophane surface the Langmuir maximum adsorption of RNA may be sufficient to give a monolayer coverage of all the available surface. Furthermore the rate at which allophane adsorbed RNA was relatively slow and took place over several hours. This could well be the result of slow diffusion of the polymer into pores and inaccessible regions in a manner similar to that observed for the adsorption of proteins.³³³

12.4 Conclusion

It has been shown that ribonucleic acid acts like a polyvalent anion in its interactions with allophane. It is adsorbed most strongly at low pH near its isoelectric point, it is displaced from the surface by pH increase and by large amounts of other anions, and it adsorbs more strongly in the presence of multivalent cations. The behaviour is also typical of a polyelectrolyte as the adsorption is intense at low concentrations and it is initially rapid, then subsequently slow.

The strength of this interaction may account for the stability of some organic compounds in allophanic soils.

The ability of allophane to bind anionic polymers, of which ribonucleic acid is an example, may help make it superior to other common clay minerals for use in effluent and water treatment.

CHAPTER THIRTEEN

THE INTERACTIONS OF ALLOPHANE WITH VIRUSES

13.1 Introduction

Over the last few decades it has been found that many different enteric viruses are present in sewage. These viruses are seldom completely removed by effluent treatment processes and so they pass into lakes, rivers, streams and estuaries. These bodies of water are frequently used for recreation and as a source of water supplies. In many cases the outbreak of viral diseases such as hepatitis and poliomyelitis has been traced to contaminated drinking water.

The use of allophane for the treatment of waters and effluents containing viruses is proposed. The work described in this chapter is aimed at showing how effective allophane might be for virus removal. Furthermore, as little is known of the fate of viruses in the natural environment this work was intended in part to determine how viruses interact with an inorganic surface.

To meet these aims an investigation of the extent of the interaction between suspensions containing allophanic clay and two viruses was carried out.

13.2 Adsorption Interactions of Viruses with Inorganic Surfaces

Viruses are colloidal particles, 20 to 200 nm diameter, of one or more molecules of DNA or RNA, usually but not necessarily covered by protein or occasionally lipid. They are able to transmit their nucleic acid to host cells and use the cell's enzyme system to bring about intracellular replication of themselves. Frequently this causes irreparable damage to the cell and if a sufficient number of cells are attacked the host organism is considered to be diseased. Because of their small size and relative inertness viruses are readily transported, difficult to detect and resistant to destruction.

As they have, in the main, surfaces of protein (sometimes also nucleic acid and lipid) viruses would be expected to have some chemical characteristics of this type of polymer. In particular their surface charges would be pH dependent with, typically, isoelectric points in the region of pH 3 to 4. It is to be expected that the adsorption behaviour of protein coated viruses will be comparable to that of the protein alone (see Chapter Eleven). For example, in neutral systems such viruses should bind firmly to positively charged surfaces. Their adsorption to other negatively charged surfaces and colloids would be weak but it could be enhanced by increasing concentrations of electrolyte and the presence of multivalent cations. The strength of any adsorption reaction would tend to be weakened at pH extremes; the presence of strongly adsorbing, highly charged anions would also prevent strong interaction. Maximum adsorption would be expected to proceed in the vicinity of the IEP of the proteins that make up the capsid, the outer shell of the virus.

These expectations have been verified by studies of the adsorption behaviour of a wide range of viruses with a number of surfaces. Reviews have been prepared by Daniels³⁶⁵ and Bitton.³⁶⁶

The rate of adsorption of viruses onto planar surfaces has been found to be controlled by both diffusion and efficiency of adsorption.³⁶⁷ The rate had a maximum, which was predicted by diffusion theory, when all collisions led to adhesion; e.g., with positively charged surfaces or with negatively charged surfaces when the electrolyte concentration exceeded a limiting value, dependent upon the charge of the cation. In dilute electrolyte, or when competing serum proteins were present, adsorption was reduced; the rate of adsorption was also reduced.

Adsorption of viruses to other colloids has generally been found to be rapid with most of the interaction taking place within one or two minutes,³⁶⁸⁻³⁷⁰ provided only a small proportion of the surface was occupied. When the amount of virus was in excess of the capacity of the surface the rate became measurably slow.³⁷¹ That the rate of adsorption by a suspended colloid was greater than that by a surface can be understood as in a suspension a virus needs to diffuse a much shorter distance to collide with a surface (see section 10.2.4).

The adsorption of viruses from near neutral solutions onto clays such as montmorillonite, kaolinite and illite, which are all negatively charged, was assisted by increasing electrolyte concentration; the salts of divalent cations were effective at one-tenth the concentration of those of monovalent cations.³⁶⁸ The valency of anions had no influence unless they were able to adsorb very strongly whereupon they were sometimes able to displace the virus. In saline waters there was an optimum salt concentration for adsorption and increasing or decreasing concentration from this point resulted in desorption. The possibility then arises of the release of viruses from estuarine sediments if they are flooded with fresh water.³⁷² Adsorption to other materials such as clays³⁶⁸ and activated carbon³⁷⁰ was also reversible and desorption could be brought

about by dilution with distilled water, addition of base to raise the pH, or addition of large quantities of substances able to bind strongly to the surface and displace the virus. Proteins were effective in this rôle.³⁷³ This procedure has found use in the recovery of viruses for analysis from large bodies of water.^{374,375} Adsorption may be directly onto membrane filters (e.g., Millipore filters),³⁷⁶⁻³⁷⁸ by polyelectrolyte³⁷⁹ or hydroxide³⁸⁰ flocs which are then collected by membrane filtration. Consistently high efficiency was obtained by acidification to pH 3 and by the addition of divalent cations such as magnesium when an iron(III) hydroxide floc was being used.

The general influence of pH is as follows. The effect of acidification of the virus suspension has usually been to bring the solution pH close to the IEP of the virus protein and maximise adsorption to most surfaces including membrane filters³⁷⁶ and clays.³⁶¹ In fact turnip yellow mosaic virus (TYMV) would adsorb onto montmorillonite from low electrolyte solution only if the pH was so close to its IEP that it was already beginning to coagulate.³⁸¹

In water and sewage treatment processes the desired effect is deactivation of viruses whether by removal or by denaturation. If destruction of the virus can be achieved with its removal, sludge treatment would become less hazardous. Typical deactivation or removal efficiencies of processes used in water treatment vary from 10 to 75% for adsorption by activated carbon,³⁸² 30% for stabilisation ponds,³⁸³ up to 98% using alum flocculation and sand filtration,³⁸⁴ 80 to 99.9% for alum flocculation with and without the presence of cationic polyelectrolytes,^{385,386} and 99.99% with cationic polyelectrolytes.³⁸⁷ Even higher efficiencies of removal or deactivation have been found using the clay mineral attapulgite although a total solids content approaching 20% was employed.³⁸⁸ The efficiency of removal, where this involved adsorption, from waste

water was found to be reduced by adsorption of other organic materials.³⁸⁶ Generally adsorption may not result in deactivation of the virus and it may be recovered unharmed. In fact adsorption by montmorillonite has retarded biological degradation of a bacteriophage (a virus that attacks a bacteria) in seawater.³⁸⁹ However a strain of poliomyelitis when exposed to an unspecified soil could not be recovered.³⁹⁰

In all their interactions with solid surfaces viruses act very much like the proteins of which their capsids are composed. They exhibit similar salt effects which enhance and inhibit their adsorption, they are bound more strongly and to a greater extent near their IEP's, they can be displaced by strongly adsorbing materials, on occasion they can be denatured and the efficiency of their removal from very dilute suspension may be very high.

13.3 Adsorption of Viruses by Allophane: An Experimental Study

13.3.1 Materials and Methods

Turnip yellow mosaic virus (TYMV) was provided by Professor R.E.F. Mathews.* Although this is a plant virus it belongs to the same virus family as the poliomyelitis viruses.³⁹¹ TYMV is icosahedral with diameter 28 nm; it has a coat or capsid of 180 identical protein sub-units or capsomers united into 20 groups of 6 (hexamers) and 12 groups of 5 (pentamers). This capsid contains the viral RNA. It is stable in strong salt solutions but it is disrupted by the presence of phenol particularly in neutral or alkaline conditions; the bonding between the proteins is thus not ionic. In weakly basic situations RNA may be lost from a virion without obvious capsid dissociation.

Reovirus type 3 radiochemically labelled with P-32 was obtained

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from Dr. A.R. Bellamy.* Reoviruses are widely distributed among human and other mammalian populations where they may be associated with minor ailments. Type 3 reovirus, like TYMV, is an RNA virus without lipid, it is icosahedral with a diameter 70 to 75 nm and it has a density of 1.36 to 1.38 commensurate with its protein content of 85%.³⁹² The rest of the virus is RNA and its total molecular weight is about 1.30×10^8 daltons.³⁹³

Prior to use both viruses were concentrated by centrifugation at 20,000 rpm at 10°C in a Sorvall RC2-B centrifuge, resuspended in 10^{-2} M sodium chloride and filtered through type HA Millipore filters (0.45 μ m). Further dilutions were made with distilled water. All apparatus that had been exposed to virus and all materials containing virus were autoclaved or washed with 20% nitric acid, before disposal or further cleaning, to destroy all remaining viruses.

The suspensions of Ohaupo allophane used were prepared in the same manner as for adsorption of protein or RNA (see section 11.5.1).

Adsorption experiments were carried out by adding 100 μ l of a suitable virus suspension to 10 ml aliquots of clay suspension in a centrifuge tube. The vessel was then closed with a rubber bung, shaken rapidly to disperse the materials and then agitated gently by end-over-end rotation at about 3 rpm. After the required time, usually 30 minutes was allowed, the pH of the suspension was determined and the tubes were then centrifuged at 2500 rpm for 20 minutes in an MSE Multex centrifuge. The supernatant liquid was then analysed for virus. For suspensions without clay no loss of virus was found unless glass vessels were employed; for this reason polyethylene apparatus was used for contact with the viral suspensions wherever possible.

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TYMV was determined spectrophotometrically with either a Unicam SP1800 or a Cary 17 spectrophotometer with 1 cm silica cells. The optical densities were recorded at 240, 260 and 310 nm and the concentration of the virus determined by comparison with standards or, if some suspended clay was present, by solution of the following simultaneous equations;

$$\epsilon_c^{260} [\text{clay}] + \epsilon_v^{260} [\text{virus}] = A^{260} \quad (13.1)$$

$$\epsilon_c^{310} [\text{clay}] + \epsilon_v^{310} [\text{virus}] = A^{310} \quad (13.2)$$

where ϵ_c^{260} and ϵ_v^{260} are the extinction coefficients of the clay and virus suspensions at 260 nm respectively, $[\text{clay}]$ and $[\text{virus}]$ are the concentrations of the two species (in g l^{-1}), and A^{260} is the absorbance at 260 nm of the sample after centrifugation.

A similar pair of equations was set up for the absorbance at 240 and 260 nm as well. It was not necessary to know the absolute values of the extinction coefficients of the clays and so the absorbances of a clay suspension subjected to the same treatment but in the absence of virus was used directly. Given that $\epsilon_v^{260} = 7.6 \text{ cm}^2\text{mg}^{-1}$ (ref. 459) the values of ϵ_v^{310} and ϵ_v^{240} were found to be 5.5 and $0.25 \text{ cm}^2\text{mg}^{-1}$ respectively.

The solutions to the pairs of equations were computed with a Hewlett-Packard 9100A calculator.

The reovirus concentration was determined by counting the beta emission from the decaying phosphorus in the supernatant liquid taken after centrifugation. This was done using a 20th Century Electronics M6H liquid Geiger-Müller tube coupled to Philips electronic counting apparatus.

The clay concentration remaining after centrifugation was determined by recording the ultra violet spectrum of each supernatant

in the region 350 to 230 nm with a Unicam SP1800 spectrophotometer, measuring the absorbance at 310 or 330 nm and comparing this with a standard curve. In the concentrations employed reovirus did not absorb significantly at these wavelengths.

For desorption studies of a clay-virus complex was prepared by equilibrating a suspension of allophane and reovirus at pH 5.6 for six hours with gentle agitation. The clay was collected by centrifugation and resuspended in distilled water, again gently agitated and recentrifuged. The clay was again resuspended in distilled water to give a suspension of 8 g l^{-1} with a count rate of about 500 counts per minute per millilitre. Aliquots of this suspension were added to samples of the various reagents again in plastic centrifuge tubes. These were agitated by end-over-end rotation for 6 hours, the clay fraction was removed by centrifugation and the activity of the supernatant determined.

13.3.2 Results

13.3.2.1 Adsorption of TYMV

The first experiments were carried out at pH 5.2 which is between the isoelectric points of the two colloids (3.75 for the virus³⁹⁴ and near 6 for the clay) where any electrostatic interaction should be strong. From a suspension of 180 mg l^{-1} TYMV, or about 1.2×10^{13} individual virions per ml, and 3.2 g l^{-1} allophane 40% of the virus was removed with the clay. This is an uptake of 2.2% by weight of the clay and would give a surface coverage of about 10% of the external surface as determined from the particle size analysis (section 3.7). Much of the surface area determined by the adsorption of nitrogen is internal; very little of this would be available for adsorption of a body the size of a virus so that the surface area estimated from the particle size distribution may be more satisfactory. When the initial

virus concentration was reduced to 30 mg l^{-1} no free virus was detected after interaction and clay removal.

In figure 13.1 the variation of virus removal by allophane with increasing TYMV concentration at constant pH and clay content is shown. (The straight line corresponds to complete removal.) The efficiency of adsorption was high for low virus concentrations but decreased when amounts large enough to cover a significant proportion of the available surface were present.

Removal of TYMV from suspension with allophane was also found to be dependent upon the pH of the system. In the region pH 4 to 7 little virus was left after the clay had been removed (fig. 13.2). Beyond this region free virus was found in the supernatant. In 10^{-2} M sodium chloride the range of the interaction was extended to higher pH. In acid system the influence was less pronounced; here the initial ionic strength was already high, the pH prior to salt addition was 2.7, so that a much larger quantity of the salt would need to be added to bring about a change.

A problem that arose in the analysis was that fluctuations were noticed in the absorbance of the clay suspensions if any conditions that influenced suspension stability were changed. Generally below pH 6 the clay was more effectively removed from suspension when virus was present but above this pH suspension stability was enhanced.

13.3.2.2 Adsorption of Reovirus

Because the reovirus was highly radioactive it was possible to use it in experiments at much lower concentrations than were used for TYMV. The loss of activity from suspension showed a similar variation with pH to that observed with the plant virus above. Again the removal was almost total in the region pH 4 to 7 when sufficient clay was present to allow rapid flocculation and consequently effective

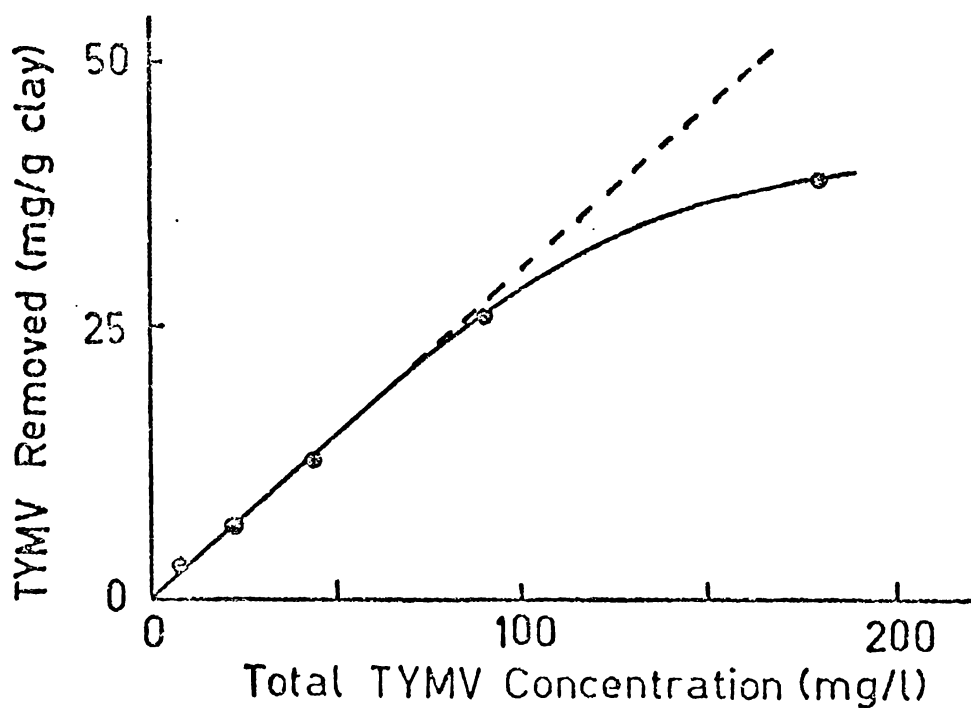


Figure 13.1. Variation of the removal of TYMV from suspension by allophane at pH 5.2 with concentration of the virus. Clay concentration 2.0 g l^{-1} .

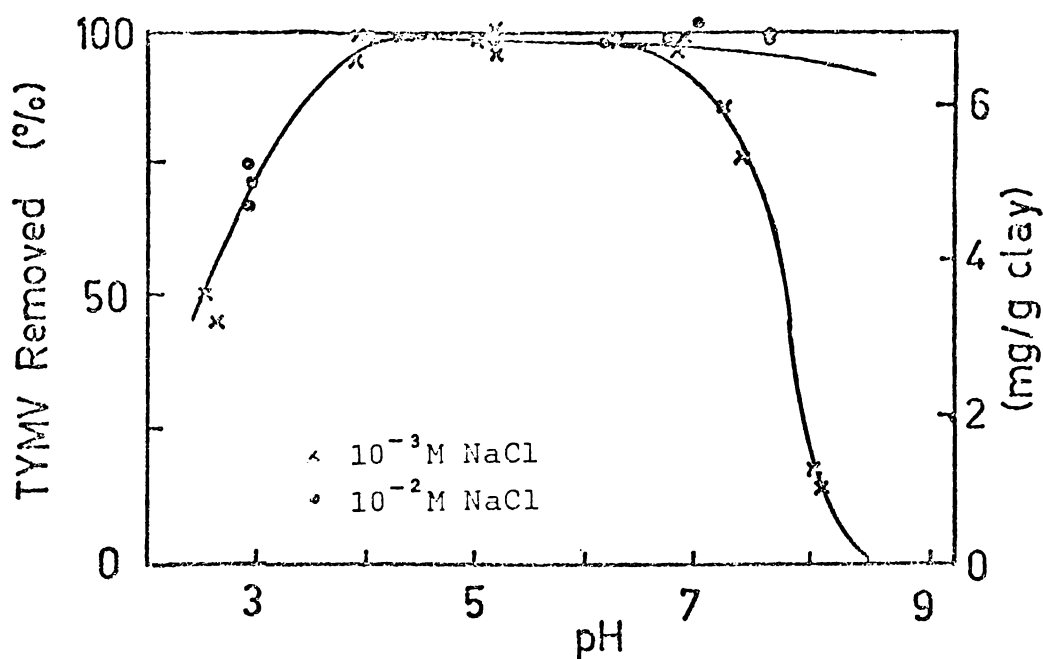


Figure 13.2. Variation of the removal of TYMV from suspension by allophane with pH and electrolyte concentration. Clay concentration 2.0 g l^{-1} .

clay removal by centrifugation (fig. 13.3). However, when the clay concentration was reduced, so that its rate of flocculation was much slower and more dependent upon the pH, reovirus removal was optimised near pH 5 (fig. 13.4). This pH is near the clay IEP but displaced toward low pH, i.e., towards the virus IEP. Between their IEP's the two colloids have opposite nett surface charges and so they would experience strong attractive electrostatic forces as well as attractive van der Waals forces (see section 10.3). At such a point their mutual interaction would be maximised.

An interesting feature found in the spectra of the supernatant liquid from the centrifugation was the appearance of a shoulder at 280 nm. The liquid had at this point an absorbance obviously greater than that due to the suspended clay alone. This shoulder was not present in the spectra of either constituent. It may have arisen from leakage of the viral RNA either through the capsid or following capsid disruption. In a virus suspension the RNA is concentrated in the virus particles; this suspension would not be as strongly absorbing as a solution in which the RNA is evenly dispersed.

To investigate the origin of this phenomenon the centrifugate obtained from the adsorption experiment carried out at pH 6.3 (which displayed this feature) was observed by transmission electron microscopy. No whole virions were found amongst the clay although some bodies which may have been ruptured capsules were seen. That the spectral shoulder was found for all the experiments carried out between pH 2.7 and 10.2 would indicate that it was caused by the clay acting upon the virus and not by pH change. Dilution with distilled water also did not produce this aberration. Furthermore reovirus recovered from dilute suspension in distilled water also appeared intact when viewed by electron microscopy. This may be taken as good evidence that the interaction of allophane with reovirus leads to

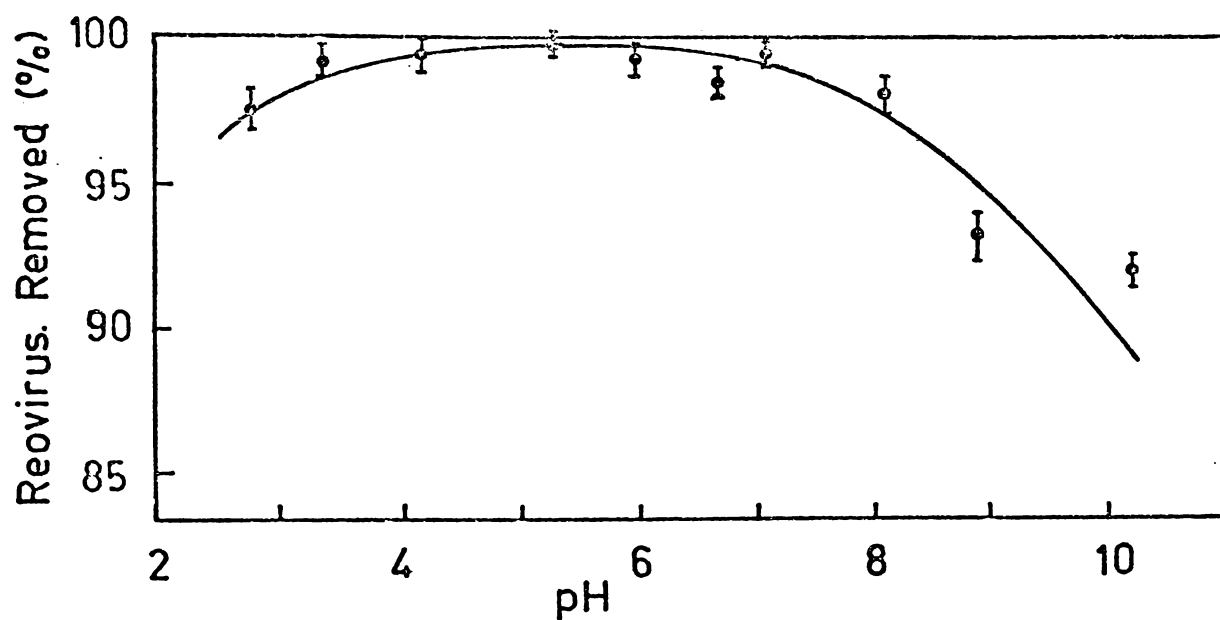


Figure 13.3. Removal of reovirus from suspension by allophane as a function of pH. Clay concentration 10 g/l.

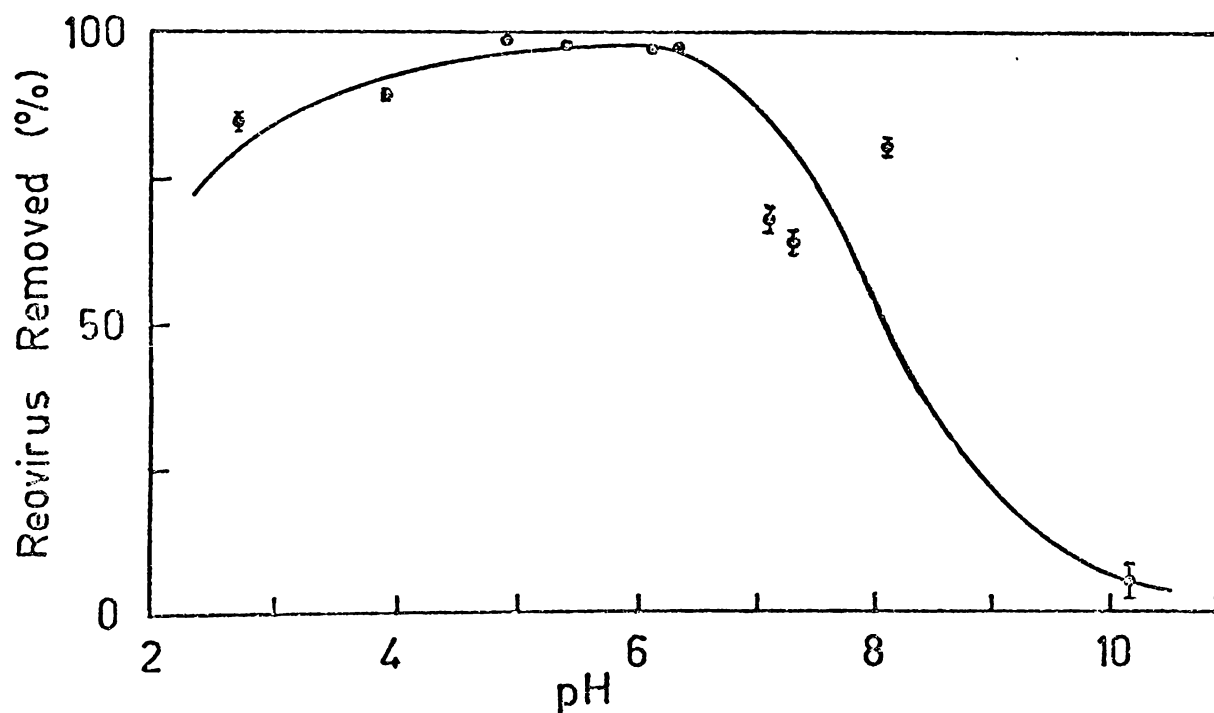


Figure 13.4. Removal of reovirus from suspension by allophane as a function of pH. Clay concentration 1.5 g/l.

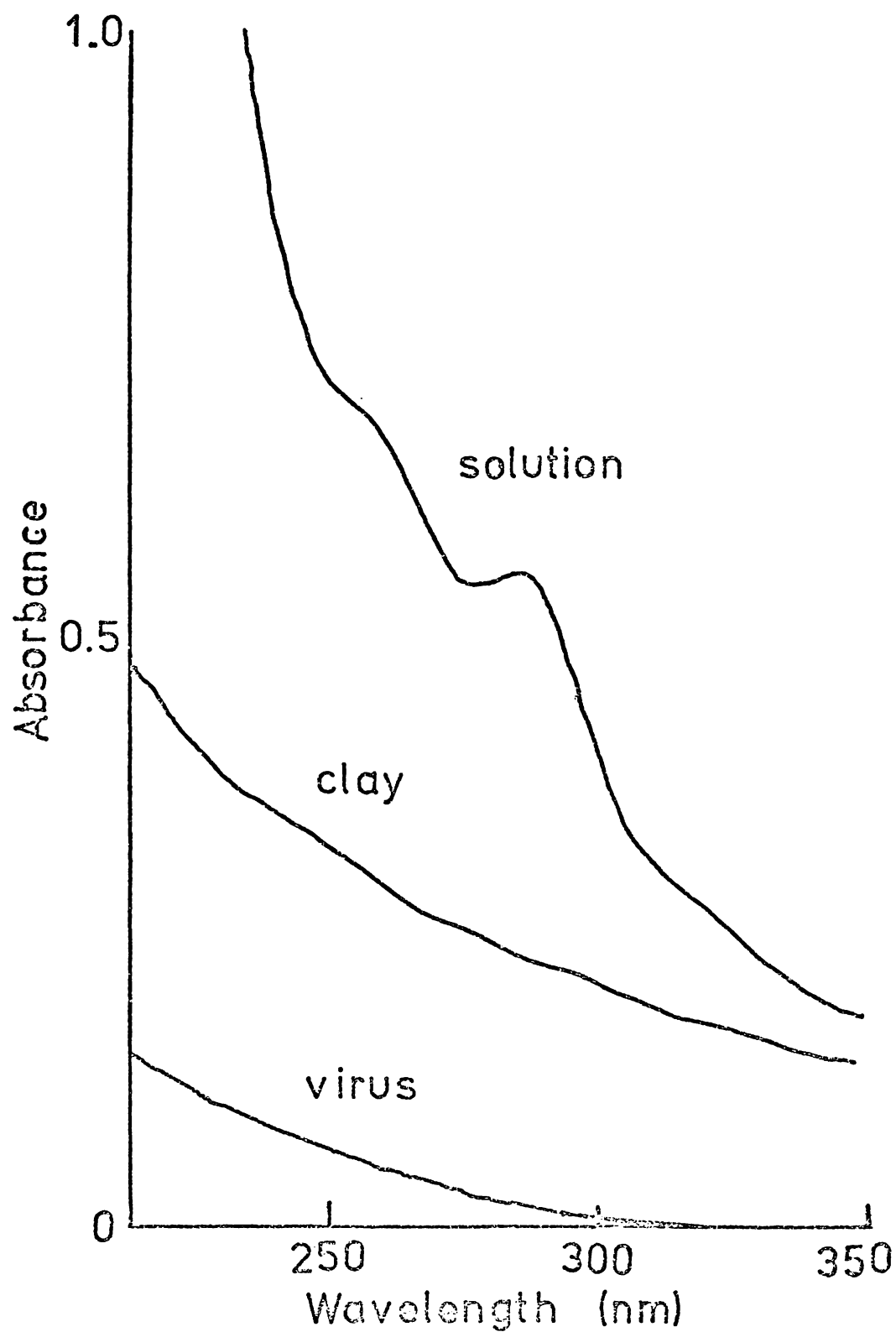


Figure 13.5. UV absorbance spectra of reovirus, a suspension of allophane and the solution recovered after interaction of allophane and reovirus. The initial concentration of reovirus in the interaction experiment was 1/20th that used to obtain the virus spectrum.

destruction of the virus and possible subsequent adsorption of the RNA by the allophane.

13.3.2.3 Desorption Experiments

The amount of radioactivity that was removed from a reovirus/allophane complex by a number of different reagents is shown in Table 13.1. The proportion of the clay that remained in suspension is also recorded.

Table 13.1 Effect of Various Reagents upon the Stability of a Reovirus/Allophane Complex

Reagent	suspended clay %	suspended label %
1 M sodium chloride	0.3	0.2 ± 0.3
5 M sodium chloride	0.2	2.0 ± 0.4
8 M urea	0.5	2.5 ± 0.4
1 M hydrochloric acid	1.0	3.3 ± 0.4
1.2 gl ⁻¹ sodium hexametaphosphate	2.6	26 ± 1
sodium hydroxide (pH 9.0)	3.6	46 ± 1
0.5 M sodium carbonate	0.5	10 ± 1
distilled water	0.1	0.0 ± 0.3

The loss of activity from the complex has been recorded in this form rather than as virus desorbed as the fate of intact virions is not known in such a situation. They may have been disrupted, they may have remained intact or they may have become denatured by some of these reagents. Nonetheless, the separation of the components bearing the radioactive label from the allophane was associated with reagents that either raised the pH or caused dispersion of the allophane by strong adsorption. Strong acid and concentrated salt solutions led to only a

small loss of activity whilst there was no desorption when the complex was suspended in distilled water.

13.3.3 Discussion

The results of this project show that when present in low concentrations TYMV and reovirus type 3 can be effectively removed from aqueous suspension by adsorption by allophane. The binding interaction occurred over a wide pH range but it was most intense at pH's between the IEP's of the two colloids. In this region the clay had a small positive charge and flocculated slowly, whilst the virus was negatively charged and stable in suspension. TYMV does not aggregate unless it is present in high concentrations whereupon it may coagulate but only at pH near its IEP.³⁸¹

In this intermediate pH region the two colloids interacted strongly together. Where it was present in sufficient concentration, i.e., in the TYMV experiments, the virus may have bridged between clay particles causing the formation of stronger and more extensive flocs. In this manner the virus would be acting like a polyelectrolyte (see section 10.2.6) or also like a colloid of opposite charge (see section 10.3). At higher pH when both colloids bore nett negative charges the nett electrostatic forces would have been repulsive and the tendency for the clay to bind the virus would have been reduced. Furthermore, at high pH the adsorbed virus would increase the nett negative charge of the clay surface and stabilise the suspension. Finally, moderate increases in the electrolyte concentration enhanced binding particularly when both colloids had the same charge.

It is apparent that adsorption of viruses by allophane is a heterocoagulation process such as that described in section 10.3.

The interaction of allophane with reovirus may be somewhat more complicated. The studies of the adsorption of this virus showed

it to behave like a colloid with a moderately low IEP. However there was no other evidence for its retention as complete virions. In fact desorption of the component of the virus bearing the radioactive label, i.e., the part that contained the nucleic acid, was remarkably similar to the desorption of RNA alone (c.f. Chapter Twelve, Table 12.1). Furthermore a material that appeared to be free nucleic acid was observed in the solution recovered after interaction. Thus it is probable that disruption of the viral capsid could sometimes occur upon its interaction with allophane particles. This would allow the nucleic acid to escape; some of this would enter the solution and the remainder would become bound to the surface.

Disruption of reovirus by allophane in this manner is of great interest. After such an interaction it is improbable that an infective particle could be reassembled as the protein fragments and the nucleic acid would either be bound to the surface or they would be widely dispersed through the solution. A further consequence of disruption would result from the nucleic acid in the solution. This material bore the radioactive label yet it was not likely to be infective. Therefore the concentration of free suspended virus would have been overestimated in these experiments. Similarly the method of analysis for TYMV also relied upon only the physical presence of viral components. In this case as well the actual virus activity may have been substantially less than the measurements would indicate. To determine the efficiency of infectivity loss, a much more relevant parameter for water purification studies, tissue culturing techniques would need to be employed. Such procedures were beyond the scope of this particular study.

Disruption of the virus and dispersion of its constituent polymers across the clay surface would also give a small amount of virus a disproportionately large impact upon the colloid properties of the clay.

This may well account for the changes observed. For instance the protection against aggregation at higher pH could result from a high degree of coating of each clay particle with anionic (negatively charged) polymer molecules. These have little tendency to aggregate themselves and so if they occupied a high proportion of the clay surface they would induce suspension stability as described in section 10.2.6.

The ease with which allophane can adsorb viruses contrasts with the activities of most other clay minerals to which strong adsorption in similar conditions generally requires relatively concentrated electrolyte solutions (see section 13.2). With reovirus, at least, the adsorption is not readily reversed; the interaction between the allophane surface and the viral components is probably much stronger because of the presence of the positive charge bearing aluminium hydroxide on the clay surface.

13.4 Conclusion

Allophane shows great promise for use as a virus adsorbent, particularly in the pH region between the isoelectric points of the virus (near pH 3) and the clay (near pH 6) where the adsorption is strongest.

There is some evidence that upon interaction with allophane viruses may be destroyed. Similar interactions with other inorganic surfaces may be an important mode whereby viruses are destroyed in the natural environment.

Because of its ability to both adsorb and inactivate viruses allophane shows further potential for use in water and effluent treatment. The resultant sludge from flocculation processes may have a greatly reduced concentration of viable pathogenic viruses and so be less dangerous to handle.

Clearly more work using procedures which assess the viability of viruses, such as tissue culturing, needs to be carried out.

CHAPTER FOURTEEN

THE INTERACTION OF ALLOPHANE WITH SMALL GREEN ALGAE

14.1 Introduction

Small algae such as *Chlorella vulgaris* are common in many exposed bodies of water. Their interactions with suspensions of allophane are of interest for two main reasons:

(i) Sewage Treatment

The treatment of sewage by low cost high rate oxidation ponds is common. In these ponds much of the organic matter from the sewage is assimilated by rapidly growing small algae whose presence is encouraged. Release of the effluents from these ponds will carry the algae into lakes, rivers, streams and estuaries where serious eutrophication may result. Recovery of the algae would not only prevent this eutrophication but also provide valuable source of food.

Growing algae in oxidation ponds or similar systems is considered to be a highly productive method of producing protein.³⁹⁵ Efficient culturing would require 1/50 the land area, 1/10 the water, 2/3 the energy, 1/5 the capital and 1/50 the human resources required in conventional agriculture to produce the same quantity of useful organic matter.³⁹⁵ On an areal basis algal cultures are more than 20, 90 and 400 times more efficient at producing protein than typical Waikato pastures, or cropping soybeans or wheat respectively.

For use as a foodstuff any recovered sludge or similar material containing algae would need to be non-toxic. This precludes the use of many polyelectrolytes and perhaps also the commonly employed aluminium salts for algal recovery by flocculation.³⁹⁶ Allophane has at least two potential advantages over these other materials; it is non-toxic, and may even be beneficial to poultry as an additive to

their food,³⁹⁷ and it may also be cheaper if it can be shown to be an efficient flocculant.

(ii) Lakes undergoing Eutrophication

Eutrophication is a process whereby a body of water becomes enriched. In a lake the inflow of nutrients usually exceeds its outflow and so there is a gradual build-up of nutrients which eventually leads to a eutrophic or nutrient rich state. If the lake looks or smells unpleasant and man has been responsible for the major portion of the nutrients causing these effects the lake is said to be polluted. Unlike rivers lakes cannot be cleaned by stopping or substantially reducing the quantities of nutrients entering them. It is necessary to remove or deactivate by some process the nutrients in the growth cycles within the lake and reduce the biomass per unit volume. Most of the nutrients are found in the microbiological and algal populations. As these are minute bodies and the volumes of water are very large conventional methods of harvesting are ineffectual. Whilst the addition of chemicals such as diquat can kill weeds, the use of algicides has been found to be impractical because of the large volumes involved and the decay of the dead organisms would release the nutrients back to the lake.

The problem that is posed here is perhaps one of colloid chemistry: how to remove the small particle fraction of the biomass from the lake body in an unobjectionable manner. A possible procedure would involve flocculation of the microorganisms so that they were deposited on the lake bottom. Provided there was a largely incomplete return of nutrients from the sediments this deposition would benefit the lake.

Allophane is known to bind firmly the major nutrient phosphate as both inorganic^{159,161,274} and organic (see Chapter Twelve) forms. As the phosphate so adsorbed is associated with aluminium, and not with

iron(III), it will not be mobilised during periods of anaerobic conditions. Allophane also adsorbs protein and other nutritious organic materials; it can also flocculate bacteria.³⁶ If it can be shown to bind other microorganisms, especially algae, it might be possible to utilise it in such a rôle in a lake.

This study was intended in part to determine whether allophane could be utilised for flocculation of small algae. *Chlorella vulgaris* was chosen as the representative organism in this instance as it is very common in natural systems, it is a major species in oxidation ponds, it is non-motile and it is small. As a consequence of its size *Chlorella* is readily maintained in suspension by minimal movement of its environment and so it has colloid properties.

14.2 Removal of Small Algae from Suspension

Two major approaches to removal of suspended algae from fresh-water systems have been made. Because of the size of the cells physical methods such as filtration and centrifugation are available but these are not always completely effective. Chemical methods rely upon the surface properties and, in fact, filtration through a sand filter as used in water treatment is probably a sorptive process.³⁹⁸ Both ion-exchange and flocculation have been shown to be efficient to varying degrees. Amongst the flocculants used have been aluminium and iron(III) salts,³⁹⁹⁻⁴⁰⁴ lime^{402,405} and polyelectrolytes.^{400,402,406,407} (Aluminium salts, especially the sulphate, are commonly referred to as alum.)

Following the discovery of the nature of the surface charge of some algae, Ives⁴⁰⁸ found that the electrophoretic mobilities of a number of them were dependent upon both the shape of the organism and the pH of the environment. Subsequently he proposed a mechanism for the flocculation of algae by aluminium and ferric hydroxides which involved mutual attraction and charge neutralisation by the negative charge bearing organism and the positive charged hydroxides, the amount of flocculant required being dependent upon the number, size and charge of the cells. A program^{ms} carried out by the Illinois State Water Survey,⁴⁰¹ although only in a narrow pH range, pH 7 to 8, gave similar results. A large number of species were observed and it was seen that the most difficult to remove were large motile flagellated algae such as *Euglena*, the same types of organism that resist retention in sand filters. *Chlorella* was also difficult to remove but not as difficult as organisms such as *Euglena*.

Neither anionic nor non-ionic synthetic polymeric flocculants have shown effective flocculation of either a *Chlorella* species⁴⁰⁷ or a mixture of algae, bacteria and other materials⁴⁰⁶ whilst in both

cases cationic flocculants were effective. In this situation an increase in the polymer molecular weight increased efficiency of flocculation but divalent cation (Mg^{2+}) and pH variation between 4 and 7 made no difference.

The most efficient flocculant studied has been alum. However, large differences have been found in the optimum amount needed for acceptable removal. Dosages of 75 to 100,⁴⁰⁰ 300 to 500,⁴⁰³ 110⁴⁰⁴ and 40⁴⁰¹ milligrams per litre have all been considered to be the minimum required amounts. The large differences may stem from differing experimental conditions, methods and criteria. In some cases the addition of polyelectrolytes has been found to benefit alum flocculation although they increase the cost of treatment and they may not be suitable for consumption by animals.^{400,403} The mechanism of flocculation by alum is similar to that proposed by Ives. As large quantities of alum are needed and the optimum pH is 5.5 where the hydroxide gel is positively charged aggregation involves neutralisation of the particle charge by surface precipitation of aluminium hydroxide and then coalescence of the hydroxide covered bodies.³⁹⁹

Magnesium hydroxide also acts in this manner if it is precipitated at pH 11 where it carries a positive charge.⁴⁰¹ Although the amount of magnesium hydroxide required was low compared with alum, 8 mg l⁻¹, a large amount of sodium hydroxide was needed to raise the pH sufficiently. Lime can also be effective but either a large quantity is needed, 500 mg l⁻¹, or some magnesium must be present to give a positively charged colloid.⁴⁰⁵ The flocculant is also temperature dependent; at lower temperatures it is more efficient.⁴⁰³

As part of an investigation of the harvesting and processing of freshwater algae Golueke and Oswald⁴⁰⁹ found almost complete removal

of a mixture of *Schendesmus* and *Chlorella* species using hydrogen-form cation exchange resins. The cells were observed to aggregate in cone shaped groups on the top of each resin bead as the suspension was passed down the column. Even though the untreated cells would only flocculate at pH less than 3.5 those cells washed from the resin would form flocs at pH 4.0. Only hydrogen form resin was effective and because of the frequent backwashing required, which consumed much acid, this method was deemed uneconomical compared with alum flocculation.

14.3 Surface Properties of *Chlorella*

Chlorella vulgaris is a small spherical unicellular green alga found in many freshwater systems including lakes, rivers and aerobic sewage ponds. Its size is variable, varying from 1.5 to 16 μm depending upon its habitat and stage of growth. The surface charge is negative over a relatively wide pH^{399, 405} and the isoelectric point (IEP) has been given as 3.0⁴⁰⁹ and 0.85.⁴¹⁰ The value of 0.85 is in better agreement with the original measurements of electrophoretic mobility and surface charge densities determined by Ives.⁴⁰⁸

The surface charges important in colloid stability will be found within a short distance of the cell surface/aqueous interface which is, for a small algal cell, either the outermost cell wall layer or, if present, the cell capsule or slime layer. The *Chlorella* cell wall has a middle layer of cellulose microfibrils and outside this an extremely resistant 14 nm thick trilaminar layer believed to consist of polymerised carotenoid material, sporopollenin a hydrocarbon. Actively growing cells tend to produce envelopes of polysaccharide mucilage either of excreted material or from gelatinisation of the outer layers of the cell membranes.⁴¹¹

Hegewald⁴¹² studied the changes in the apparent zeta potential

with life cycle of *Chlorella fusca* and concluded that it was a function of the cell excretions and not of the cell wall. Thus the charge at the cell surface will originate in the polysaccharide mucilage from ionisation of acids such as D-galacturonic and D-glucuronic acids known to be in the slime layer.⁴¹³ As these acids have quite low acid dissociation constants, pK_a near 3.5,¹⁴⁶ ionisation will be complete at quite low pH values and so in the absence of weakly acidic or basic groups there will be no tendency for the zeta potential to change in the moderate pH regions. At constant pH Shcherbakova^{414,415} found zeta potential variations within the same culture, particularly if the growing conditions were not favourable.

14.4 Adsorption of Polysaccharides

The external surface of most microorganisms controls their adsorption and adhesion behaviour.^{365,366,416} This can be expected to be so for *Chlorella* as well. As this organism has a covering of polysaccharide it is this material that will dominate its surface properties.

Polysaccharides are condensation polymers of glycosidically linked monosaccharides. They generally contain more than ten sugar residues which may be of only one type or of several.⁴¹³ Polymers of simple sugar derivatives are usually included in this classification. Some examples include cellulose, a polymer of glucose, the alginates, polymers of sugar amines, and plant gums which are neutral salts of branched acidic polysaccharides that usually contain glucuronic acid. The adsorption interactions of these substances have not been at all extensively studied; for instance, no reports of their interactions with hydrous oxides are available. However, as they influence soil structure⁴¹⁷ their interactions with some of the clay minerals,

especially montmorillonite, have been investigated.

Some similarities between the adsorption of polysaccharides and their sugar or sugar derivative monomers have been found. In general the presence of a functional group gives both polymer and monomer a similar dependence upon external influences. If such a group is ionisable it will dominate the adsorption process and dictate the influence of pH and electrolytes.^{317,418} Thus amine groups bring about adsorption by cation exchange.⁴¹⁹ This is most pronounced for clays bearing labile cations such as sodium. The adsorption of sugars with acid groups shows similarities to the adsorption of other anions and clays saturated with highly charged cations are more active adsorbents. Thus both calcium and aluminium have been found to enhance adsorption of such compounds,^{419,420} whilst for an extract of soil polysaccharides adsorption by kaolinite increased in order of the saturating cation: $\text{Na}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{H}^+ < \text{Al}^{3+} < \text{Fe}^{3+}$.⁴²¹ Plant root mucigel, also a polysaccharide, binds strongly to clay mineral surfaces possibly by an interaction between adsorbed aluminium and the carboxyl groups of the organic part.⁴²²

The adsorption of a polysaccharide derived from a bacteria was found to occur in the interlamellar regions of montmorillonite and so it was dependent upon the strengths of the interactions between the layers.⁴²³ Thus it was readily replaced by strong solutions of sodium sulphate; the sodium being a weakly aggregating and anion-binding cation and the sulphate, upon adsorption, enhancing the clay negative surface charge and the repulsion of the negatively charged acid sugars.

It can now be seen that the slime layer of *Chlorella*, which is composed of polysaccharides containing acidic carboxyl groups, can be expected to interact with allophane, an aluminosilicate material with a surface partly composed of polymeric aluminium hydroxide.

14.5 The Interaction of *Chlorella vulgaris* with Allophane: An Experimental Study

14.5.1 Growth and Preparation of *Chlorella*

A sample of *Chlorella vulgaris*, isolated from the Auckland Regional Authority sewage treatment plant at Mangere, was obtained from Professor V.J. Chapman,* smeared onto sterile plates of algal nutrient agar** and allowed to grow in light for one week at 25°C. Pure colonies were isolated and transferred to sterile algal culture medium** in Pyrex flasks plugged with non-absorbent cotton wool and these were exposed to fluorescent light. (When available a shaker bath thermostatically maintained at 27°C was used.) Fresh cultures were prepared every two or three days by transferring algae to fresh sterile media using sterile techniques. The occurrence of bacterial contamination was found by plating a few drops of actively growing samples on nutrient agar and incubating for 24 hours at 37°C. If bacteria were found the algal culture was discarded. In this way axenic cultures were maintained for several months. Only actively growing cultures were used for experiments; old cultures were used to seed fresh media or discarded.

Before use in experiments the algae were collected by centrifugation at about 100 g for 5 minutes and washed 5 times with particle-free distilled water (obtained by drawing distilled water through 0.2 µm Millipore filters). The final precipitate was resuspended and allowed to stand for one hour per 5 cm depth; this allowed large particles and clumps to settle out. The remaining suspension was removed and diluted to the required concentration with Millipore filtered distilled water. The particle size distributions

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**The composition of the algal nutrient agar and the algal nutrient medium are described in Appendix V.

of the suspension used for the experimental studies and the actively growing *Chlorella* are discussed in Appendix VI.

14.5.2 Interaction of Allophane and Chlorella

Suitable aliquots of clay suspension, previously equilibrated at various pH's as described in section 10.5.2, were taken in 100 ml glass beakers. When necessary, electrolyte and particle-free distilled water were added and the mixture was stirred for 5 minutes at 150 rpm with a bar stirrer. An aliquot of algal suspension was then added to give a final known volume of 50 to 70 ml. Stirring was continued at 150 rpm for one minute and then at 20 rpm for 14 minutes; slow stirring being beneficial to floc formation by such large bodies (see section 10.2.4). After standing for 30 minutes, a 10 ml aliquot was withdrawn from a depth of 2.5 cm, the clay concentration determined by measurement of its optical density (see section 10.5.2) and the algal content determined as described below. Only in highly concentrated suspensions did the algae have a significant optical density; this was corrected for by independent measurements on suitable blank samples.

14.5.3 Determination of Chlorella Concentrations

An Ab Lars Ljungberg Celloscope 401 fitted with an 80 μ m orifice was used to determine the algal concentration. This instrument applies a constant electrical potential through an orifice immersed in an electrolyte solution. When particles are drawn through the orifice the electric current is disturbed by an amount proportional to the particle volume. If the pulse is greater than a predetermined size it is counted.

Differentiation of dispersed clay and *Chlorella* cells was facile, the algal cell volume being about 10-20 times that of a larger clay

particle volume. The recommended electrolyte (1% sodium chloride) flocculated the relatively small clay particles and resulted in groups of these having volumes large enough to register counts even when the pulse size discriminator was set at maximum. An electrolyte which would maintain any clay in a dispersed form was then necessary. A solution of 7.0 g sodium carbonate, 3.0 g sodium bicarbonate and 1.20 g sodium hexametaphosphate per litre, which is buffered at pH 10.0 and has an ionic concentration near that of 1% sodium chloride, was found suitable. A concentrated form of this mixture was prepared and suitable aliquots added to suspensions prior to counting. (Where possible, all liquids were filtered through Millipore type GS (0.22 μm) filters.) Under these conditions, provided the clay concentration was less than about 0.2 g l^{-1} there was little interference from the clay. Above this concentration either dilution or blank preparation was employed. Dilutions were also made if the algal concentration exceeded $40 \mu\text{l}^{-1}$ otherwise coincidence (i.e., simultaneous entry of two or more particles into the orifice) gave low readings.

14.5.4 Results and Discussion

14.5.4.1 *Chlorella* Suspension Stability

The large size of *Chlorella vulgaris* in colloidal terms and the fact that it is more dense than water makes it liable to sediment moderately rapidly in quiescent suspensions. To be sure the effects observed were independent of this sedimentation it was necessary to withdraw samples for analysis from the suspension at a time and from a position such that the suspension concentration was apparently unchanged after the cessation of stirring. In figure 14.1 the cell concentration of *Chlorella* for the standard sampling position, 2.5 cm below the liquid surface, has been plotted against the time after

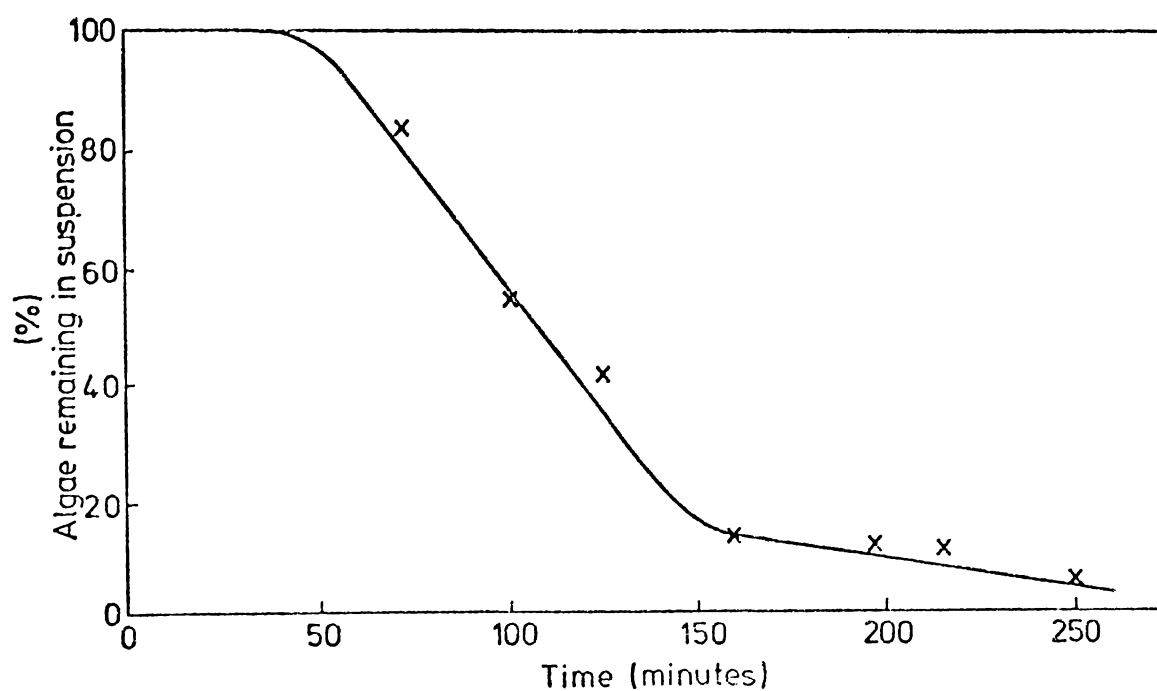


Figure 14.1. Removal of algae from suspension by ~~sedimentation~~ ^{sedimentation} ~~allophane~~ as a function of time. Clay concentration 3.0 g/l; algal concentration 1.8×10^8 per litre.

stirring was halted. As there was no significant change in the cell concentration until after 40 minutes, if any additive caused a change within 30 minutes it was considered to be significant.

The slow stirring alone did have an influence upon the amount of suspended material. In general about 40% of the algae were removed from suspension by this process alone and so for all experiments blank samples of the algal aliquot suspended in the liquid medium being used were prepared and their concentrations determined. These were used as the base values. The precipitated algae were aggregated under the centre of the stirrer and it is suggested that as the cells were swept along the vessel bottom in the absence of strong stirring the sedimentary velocity may have exceeded the suspending turbulent velocity and allowed precipitation of the cells. This material could be resuspended by rapid stirring and gave the same amount of precipitation upon repetition of the process.

Flocculation of *Chlorella* alone was attempted at various pH's and electrolyte conditions but only below pH 3, when the cells changed colour and were probably denatured, did any floc formation occur. The amount lost from suspension in this case was only 65%. *Chlorella* was suspended in a number of electrolyte systems, including 10^{-1} M NaCl, 10^{-3} M Na_2SO_4 and 10^{-3} M CaCl_2 , at pH 5 to 6 but none effected flocculation of the suspension. These results and the observed electrophoretic behaviour of *Chlorella*^{399,408,414} are indicative of it being a highly negatively charged body and not readily flocculated by itself. This is not to be unexpected as it depends upon being widely dispersed in natural waters; ready aggregation would not allow it to be such a successful organism.

14.5.4.2 Influence of Allophane upon *Chlorella* Suspension Stability

The addition of allophane was observed to have profound

influences upon the stability of *Chlorella* suspensions. In figure 14.2, which shows the results of experiments carried out at low electrolyte conditions, the ordinate expresses the amount of material remaining in suspension 30 minutes after the cessation of stirring as a percentage of the amount added, in the case of the clay, or, for the algae, as a percentage of the amount found in suspension for a sample without flocculant. The flocculation efficiency is thus directly comparable to sedimentation of the individual cells.

The pH for maximum removal of the algae is seen to coincide with the pH for maximum clay flocculation, although algal removal was more efficient at all pH's. It is particularly notable that there was some precipitation of the algae at pH 7 where suspensions of both components alone were stable. Similar results were obtained with a less concentrated clay suspension which had a slightly higher IEP (pH 6.0); these are given in figure 14.3.

Addition of electrolyte was found to enhance flocculation of the *Chlorella* but it apparently does this by the effect it has upon the clay alone as the algal removal was related to the efficiency of flocculation of the clay. Sodium chloride extended the pH range of flocculation (fig. 14.4); sodium sulphate was less effective at higher pH than sodium chloride (fig. 14.5); and calcium chloride was particularly effective at higher pH (fig. 14.6). The restabilisation at pH 5 for calcium was probably due to adsorption of this divalent cation which would raise the nett surface charge so that the nett interparticle repulsive forces became significant.

The results of two further experiments where the flocculation was studied for varying amounts of clay are of interest. The first of these was followed by counting the particle concentration as above; in figure 14.7 it is seen that the efficiency of flocculation at pH near 6 increased with clay concentration. At the same time the clay

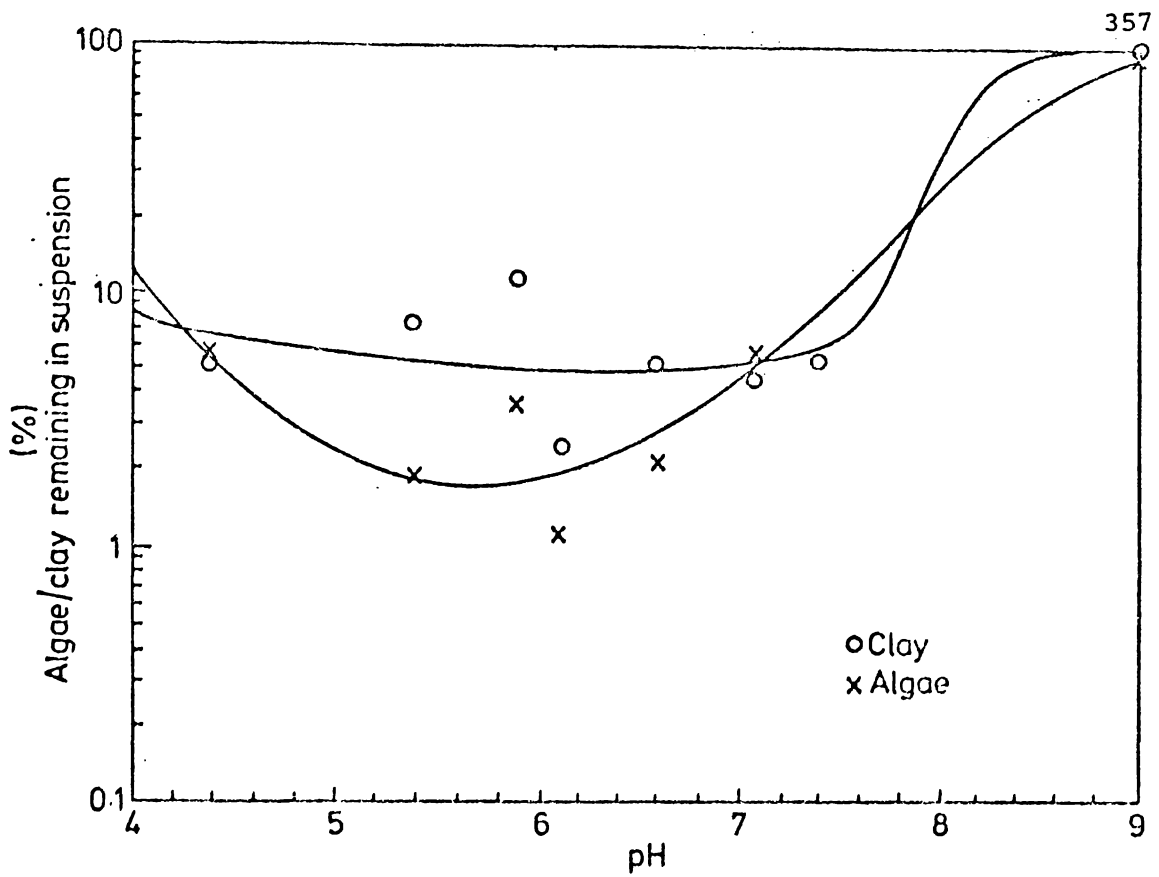


Figure 14.2. Removal of algae from suspension by allophane as a function of pH. Clay concentration 1.0 g/l. Algal concentration 1.8×10^8 per litre.

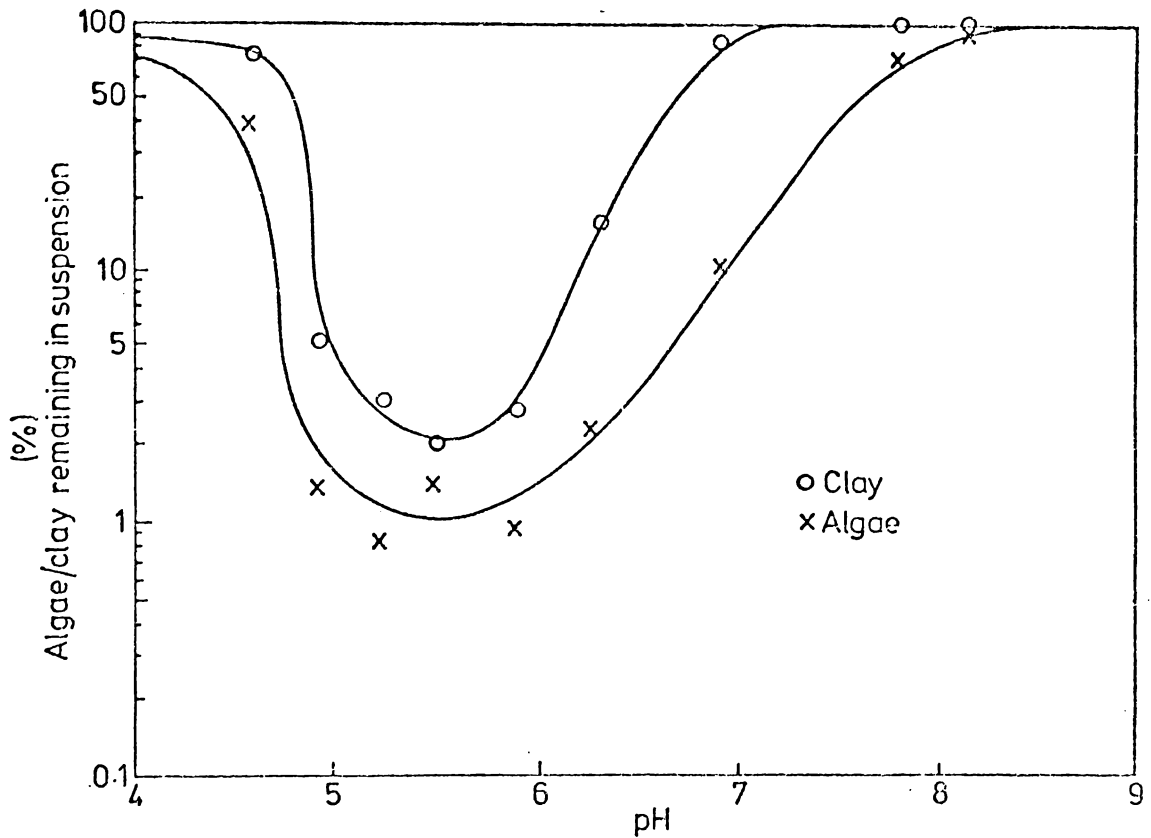


Figure 14.3. Removal of algae from suspension by allophane as a function of pH. Clay concentration 3.0 g/l. Algal concentration 1.8×10^8 per litre.

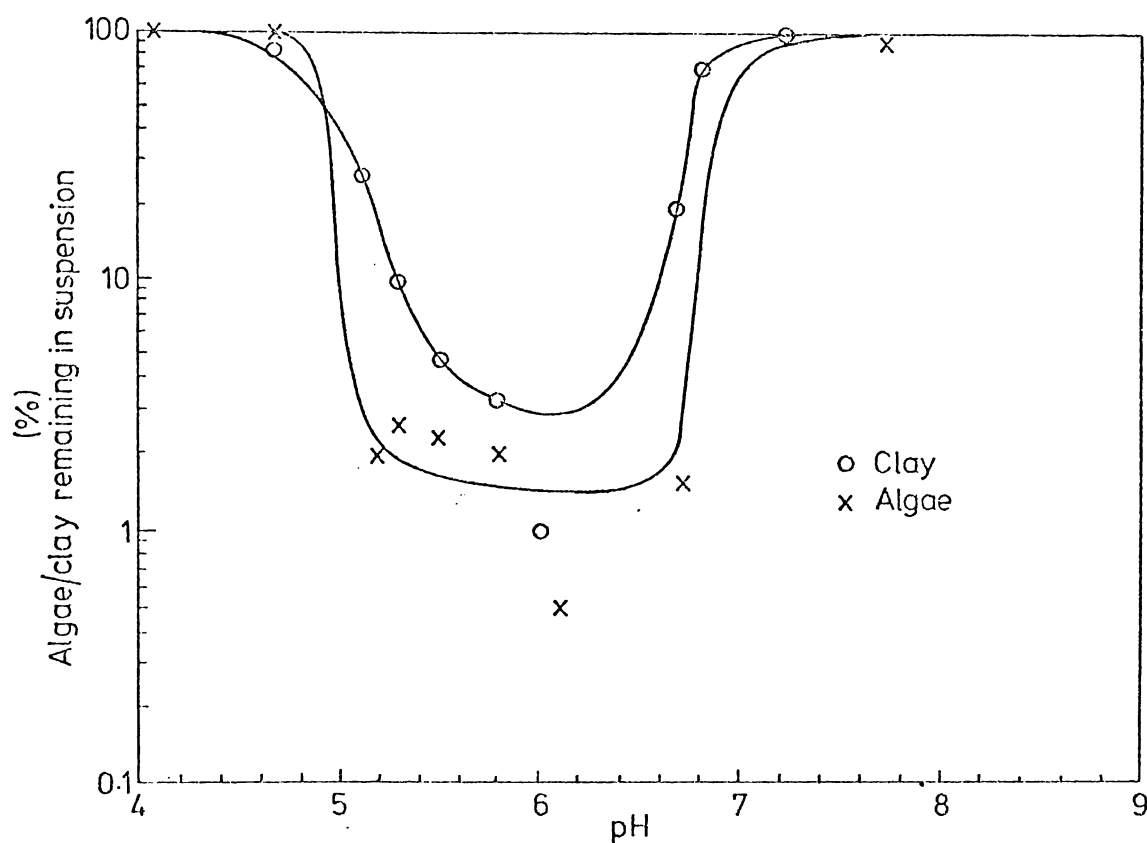


Figure 14.4. Removal of algae from suspension by allophane as a function of pH in $10^{-2}M$ sodium chloride. Clay concentration 3.0 g/l; algal concentration 1.8×10^8 per litre.

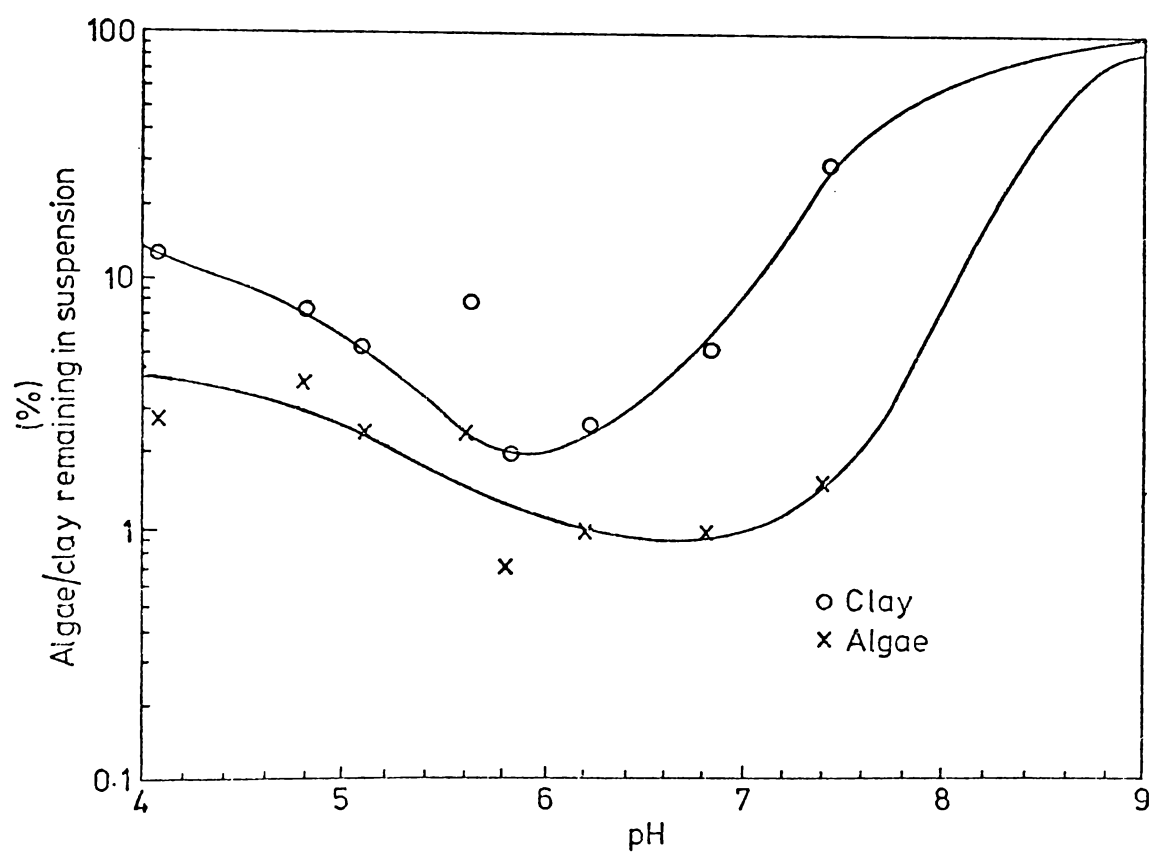


Figure 14.5. Removal of algae from suspension by allophane as a function of pH in 10^{-2} M sodium sulphate. Clay concentration 3.0 g/l; algal concentration 1.8×10^8 per litre.

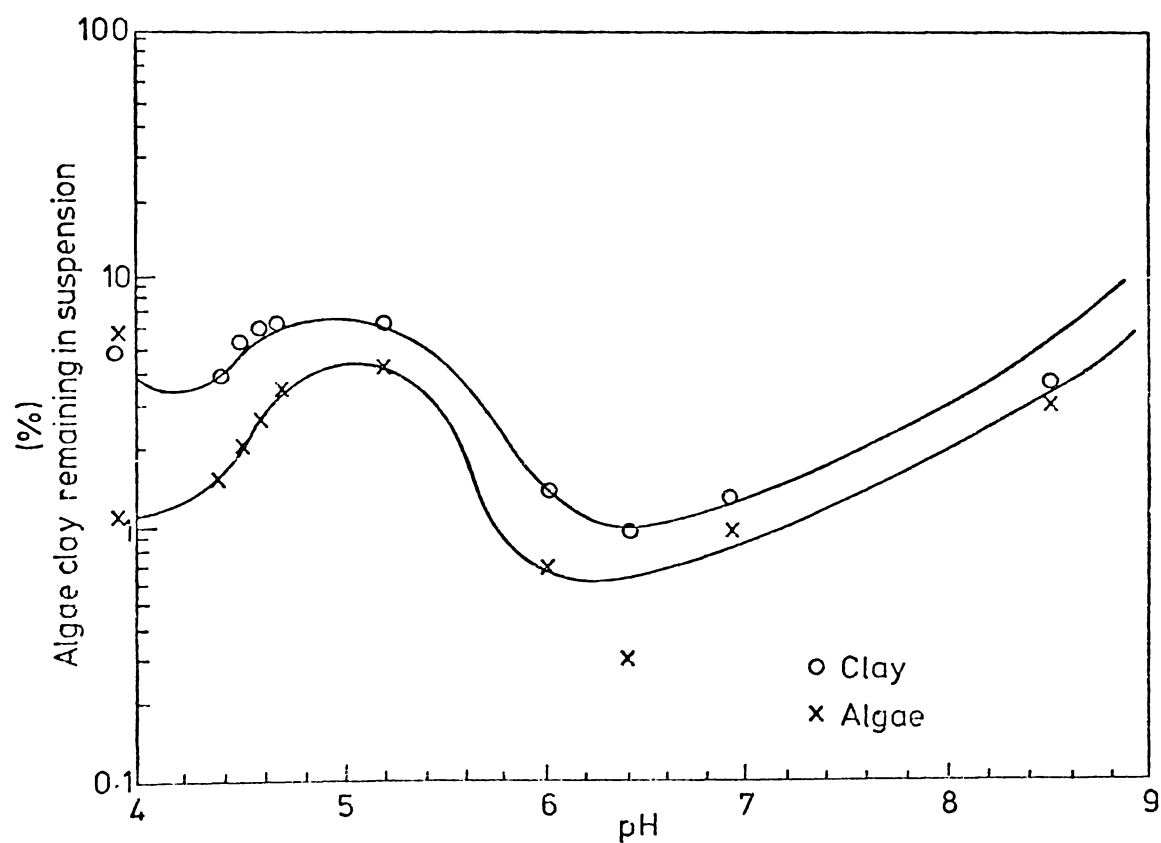


Figure 14.6. Removal of algae from suspension by allophane as a function of pH in $10^{-2}M$ calcium chloride. Clay concentration 3.0 g/l; algal concentration 1.8×10^8 per litre.

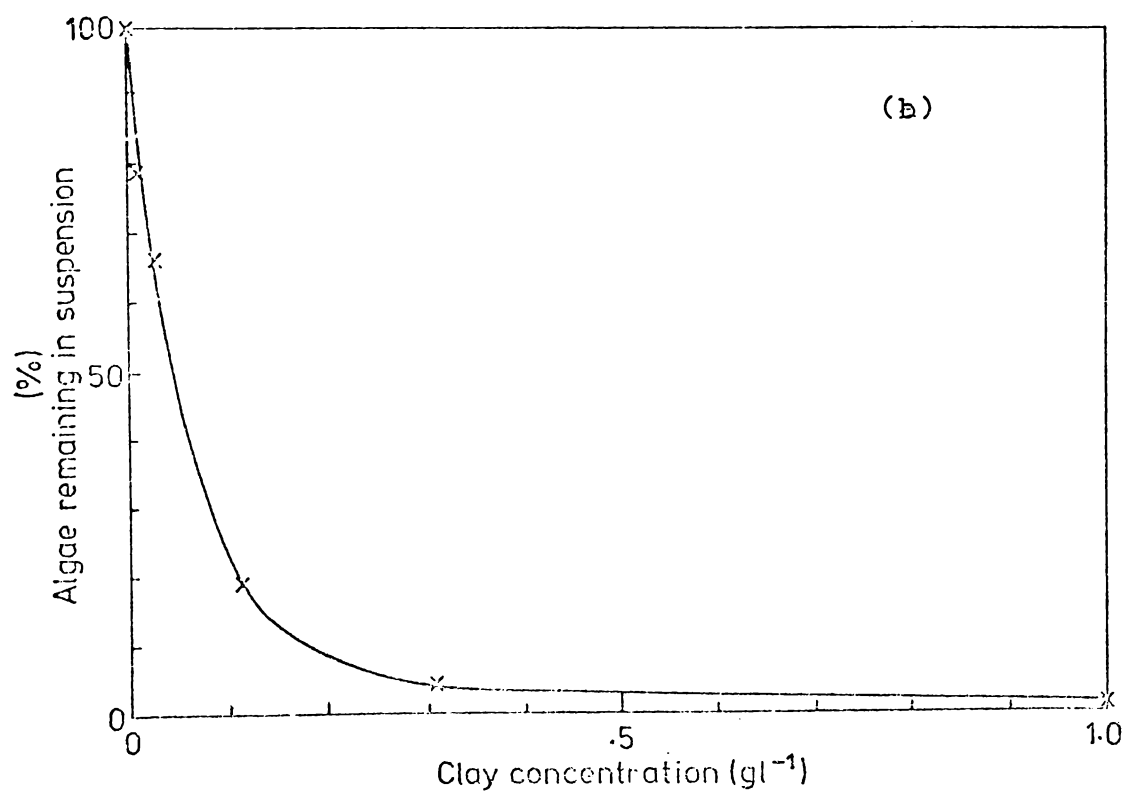
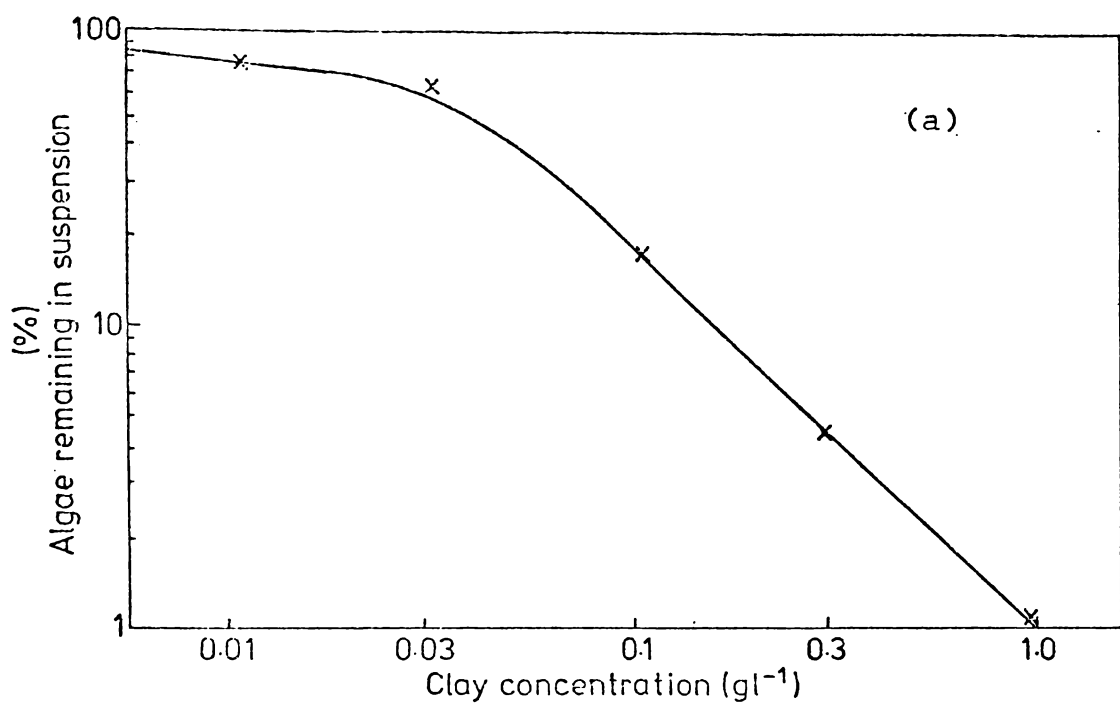


Figure 14.7. Removal of algae from suspension by allophane as a function of clay concentration at constant pH (near pH 6). Algal concentration 1.8×10^8 per litre.

flocculation also increased although it did not lead to sedimentation at low concentrations because the flocs formed were too small (see Chapter Ten). For the second experiment the extent of flocculation at pH near 7.2 was followed by microscopic observation and recorded photographically using a Reichart Zetopan microscope and Braun Paxette camera.

The first two photographs, Plates 14.1 and 14.2, are of dispersed and coagulated allophane respectively. There is a marked difference between the two states; the dispersed clay particles appear to be diffuse grey circles with white centres, well separated, whereas the flocs appear to be aggregates of more definite bodies. The third photograph, Plate 14.3, shows some freshly grown algae including both juvenile (small) and mature (large) cells. The surfaces of these are quite smooth and the spherical nature of the cells is obvious.

Addition of allophane again was highly influential upon the state of the dispersed algae even at pH 7.2 where both isolated suspensions were stable. The first indication of cell aggregation in a suspension of 1.5×10^6 cells per ml was when 2 mg per litre of clay had been added. At 10 mg l^{-1} addition floc development was extensive and as shown in Plates 14.4 and 14.5 most cells were aggregated. A large proportion of the cells were coated with clay particles which gave their surfaces a roughened appearance. These adsorbed clay particles also seemed to be uniting the cells. Only a very few free clay particles were observed in the suspension. With an increase in clay concentration from 30 mg l^{-1} to 1 g l^{-1} there was a change in the nature of the flocs (Plates 14.6 to 14.9). More and more clay became apparent in the flocs and in the suspension and the algal cells became progressively separated by clay until at high clay concentrations the *Chlorella* appeared to have been enmeshed in clay flocs. The most efficient dosage was observed visually to be 300 mg l^{-1} and there all



Plate 14.1. A stable suspension of Ohaupo clay. (x 600)

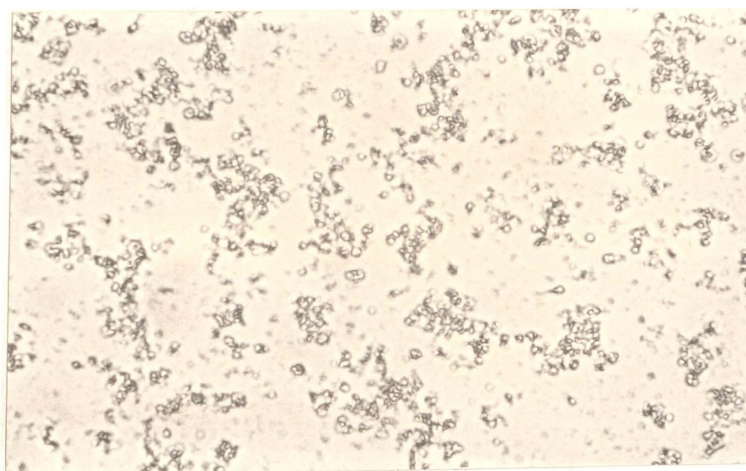


Plate 14.2. Coagulated Ohaupo clay. (x 600).

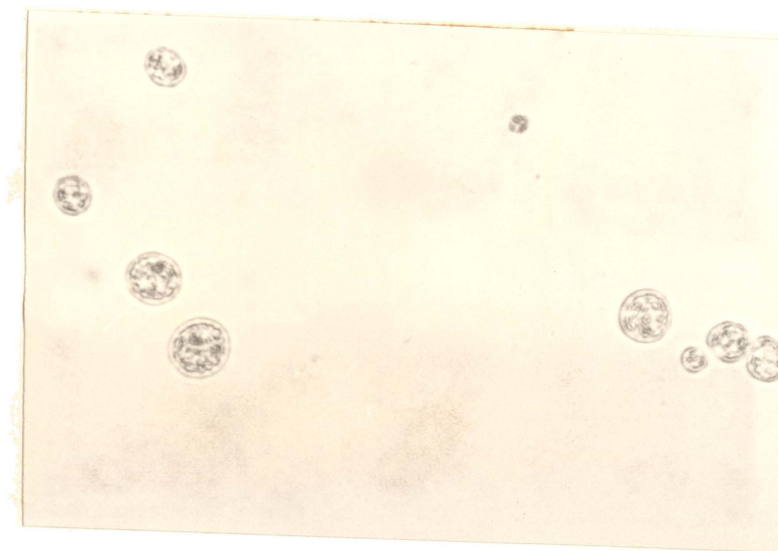


Plate 14.3. *Chlorella vulgaris*. (x 600)

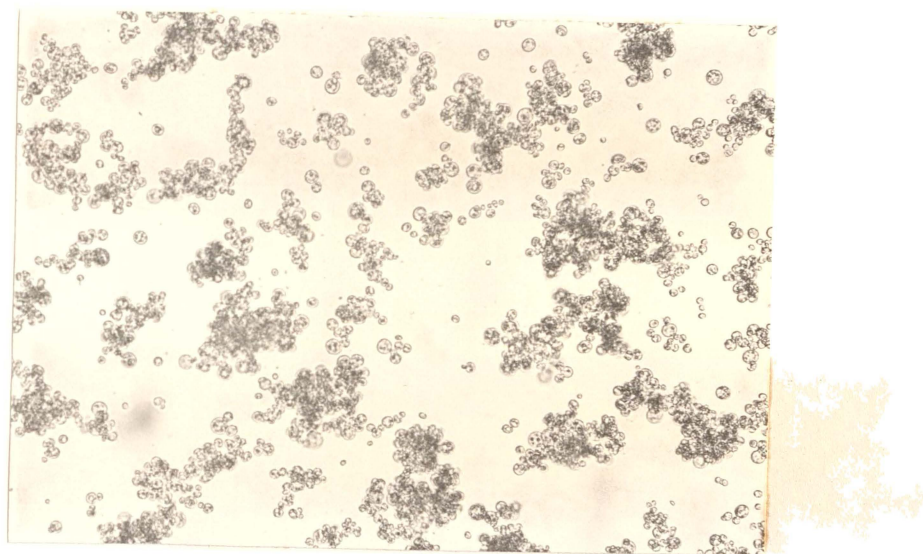


Plate 14.4. Flocculation of *Chlorella vulgaris* by allophane. Algal concentration; 1.5×10^9 per litre. Clay concentration, 10 mg per litre. (x 150)

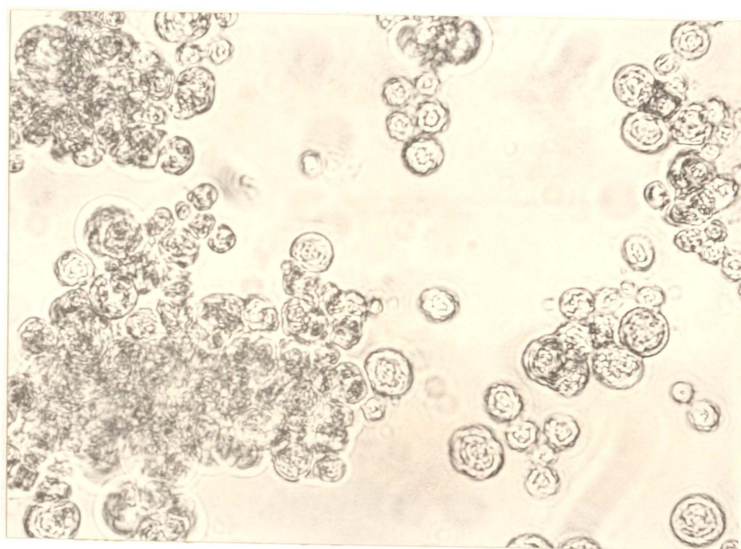


Plate 14.5. Flocculation of *Chlorella vulgaris* by allophane. Algal concentration 1.5×10^9 per litre. Clay concentration, 10 mg per litre. (x 600)

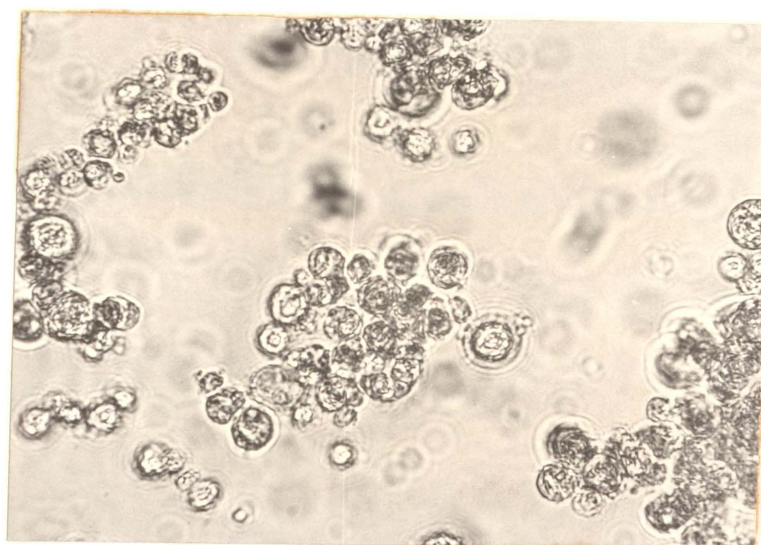


Plate 14.6. Flocculation of *Chlorella vulgaris* by allophane. Algal concentration 1.5×10^9 per litre. Clay concentration 30 mg per litre. (x 600)

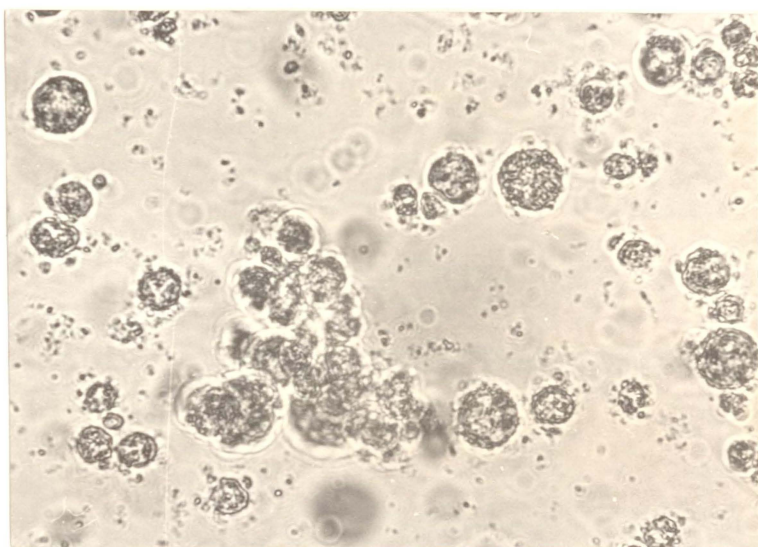


Plate 14.7. Flocculation of *Clhorella vulgaris* by allophane. Algal concentration 1.5×10^9 per litre. Clay concentration 100 mg per litre. (x 600)

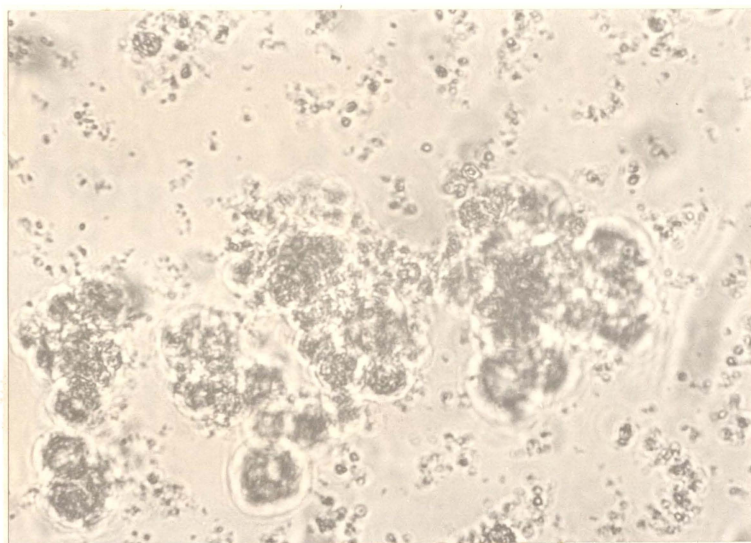


Plate 14.8. Flocculation of *Chorella vulgaris* by allophane. Algal concentration 1.5×10^9 per litre. Clay concentration 300 mg per litre. (x 600)

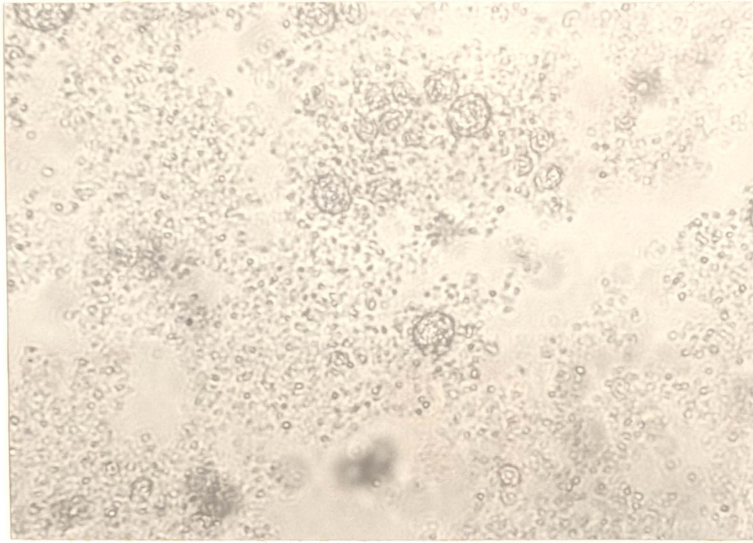


Plate 14.9. Flocculation of *Chlorella vulgaris* by allophane. Algal concentration 1.5×10 per litre. Clay concentration 1.0 gram per litre. ($\times 600$).

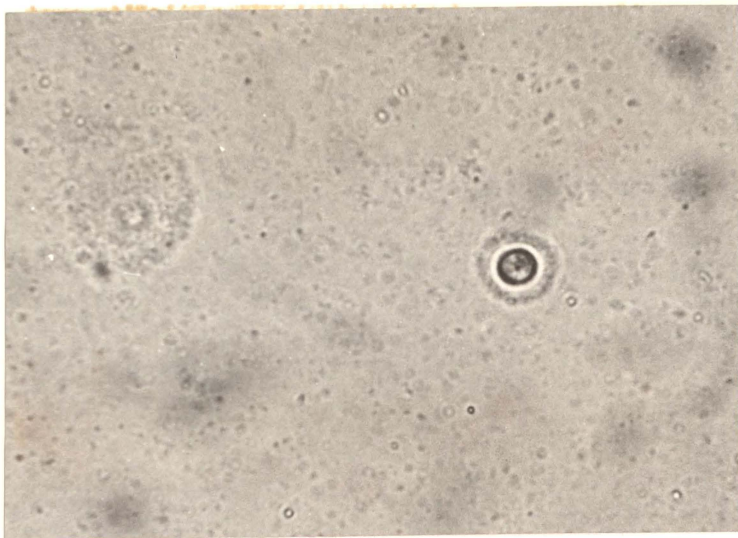


Plate 14.10. Aggregation of allophane about a single cell of *Chlorella vulgaris*. A floc of allophane alone can be seen to the right of the plate.

cells were part of a floc. Finally Plate 14.10 shows a solitary algal cell in a stable concentrated allophane dispersion at pH near 7.5. The cell appeared to have drawn a coating of clay about 3 μm thick about it in which the clay particle concentration was much greater than in the bulk suspension. The clay in this coat appeared to be in a flocculated state. (A floc is visible to the right of the micrograph.)

14.5.4.3 Nature of the *Chlorella*/Allophane Interaction

There are two possible causes for the interactions observed between the clay, allophane, and the *Chlorella* cells observed in this study.

In Chapter Ten heterocoagulation between dissimilar bodies was discussed and it was seen that it was possible such bodies stable in independent suspensions may interact and mutually aggregate. The conditions necessary were either that the two types of particle had opposite surface charges or there were very large differences in their effective surface potentials. At pH less than 7 the allophane surface potential would be relatively small and it would become less negative from pH 7 to 6, it would be zero at the IEP (near pH 6) and then increasingly positive with further decreasing pH. As the *Chlorella* has a very low IEP strong interaction between the two bodies would be expected over the region between the two IEP's with a maximum intensity at a pH such that the clay bore a nett positive charge, perhaps near pH 5. For there to be a heterocoagulation type of interaction at pH 7.2 there would need to be a large difference in the effective surface potentials. From Chapter Nine, assuming that the clay particle was a uniform sphere of diameter 1 μm with an em of $1.4 \mu\text{m sec}^{-1} \text{cm V}^{-1}$, it would have a zeta potential of - 18 mV. For various *Chlorella* suspensions potentials of - 8,³⁹⁹ - 20,⁴⁰⁷ and

- 26 mV⁴⁰⁵ have been reported. Whilst these potentials are low enough to perhaps lead to some aggregation the nett interactions at most separations will tend to be repulsive; they are not sufficiently different for the possibility of attractive Coulombic interactions at close approach. Furthermore, this type of aggregation would lead to the adsorption of only single layers of clay particles and not the thick blanket observed in Plate 14.10. That Coulombic forces are not responsible can be deduced from consideration of the double layer thickness as measured by the Debye length parameter, κ^{-1} . In 10^{-4} M sodium chloride, the electrolyte used for the suspension shown in Plate 14.10, the effective double layer thickness would be (section 4.5.2) only about 30 nm or about 1% of the thickness of the allophane blanket seen here. The clay-algal interaction could then be expected to involve only single layers of either particle. It is unlikely that the aggregation of *Chlorella vulgaris* by allophane is the result of simple particle-particle interactions.

The second possible mode of interaction may involve the adsorption of the acidic polysaccharides of the algal cell slime layer onto the clay particles. In section 13.4 it was seen that polysaccharides have been known to bind strongly to clay minerals onto which aluminium in particular had already been adsorbed. In previous parts of this thesis it was shown that discrete polymeric aluminium hydroxide or hydrous oxide is a major part of the allophane surface and that allophane binds anionic organic polymers such as RNA firmly. Thus it would not be unreasonable to expect the algal cell slime layer constituents to adsorb onto the allophane surface even when the clay is to some extent negatively charged. The outer part of the slime layer is always slowly being lost from the cell. As polymers become free they will be able to adsorb onto already bound clay and bridge to further allophane particles building up a clay blanket about the cell.

In this manner allophane particles may act as bridges between cells and polysaccharides may bridge between clay particles allowing the formation of massive clay-algae conglomerates.

In the presence of large excesses of free clay the flocculation of these bodies will act in the same manner as the flocculation of the clay alone. Thus conditions such as suitable pH or the presence of high electrolyte concentrations will lead to an increase in the efficiency of algae removal from suspension. As these conglomerates are more massive and every cell is part of a significant floc, cell removal will be more efficient than clay removal, all clay particles not necessarily being aggregated. Support for this mechanism at high clay concentration was obtained from an experiment carried out at pH 5.6. Various quantities of *Chlorella* were added to suspensions of allophane of constant concentration (1.0 g l^{-1}). There was little fluctuation in the percentage of the amount of either the clay or the algae remaining in suspension after flocculation had proceeded for 30 minutes.

Because of the ease of floc formation it is possible that the degree of algal removal from suspension was not necessarily related to flocculation efficiency but instead to the rate of sedimentation. The flocs formed with only a small amount of clay and a large amount of *Chlorella* would not have densities greatly different from that of the suspending medium. Consequently their sedimentation would be slow. With a higher clay concentration the relative density would be greater and the sedimentation more rapid. The influence of allophane concentration upon the kinetics was not investigated; nor were the effects upon floc strength which may also be important in any large scale process.

The onset of efficient flocculation was found to occur at a clay concentration of between 10 and 30 mg per 1.5×10^9 cells. As the

algae was found to have a total dry matter content of 6.5% by weight (see Appendix VI) upon drying the floc formed at this relative concentration would contain approximately equal quantities of clay and algal residues.

14.6 Conclusion

It has been shown that the clay mineral allophane is able to interact strongly with the small green alga *Chlorella vulgaris* and cause it to be removed by sedimentation from quiescent suspensions. The mechanism of interaction appeared to be by adsorption of polysaccharides from the algal slime layer by the clay. This lead to aggregation into rapidly sedimenting flocs. If the clay was present in sufficient concentration to liberally coat the cells the resulting suspension flocculated in a manner like the clay alone. The removal of the algae was generally more efficient as each cell more readily became a part of a floc because of its size and high probability of collision with clay bodies; not all clay particles would be so readily involved in collisions leading to aggregation.

Under the experimental conditions employed onset of flocculation was observed following the addition of 2 mg clay per 10^9 cells. The efficiency increased with clay concentration. A realistic procedure to induce flocculation might be to add about 20 mg clay per 10^9 cells; this is approximately equal weights of allophane and algae on an oven-dried basis.

Flocculation of small alga by allophane has a similar efficiency to flocculation by magnesium hydroxide or aluminium salts. It is less efficient than the use of aluminium salts in conjunction with polyelectrolytes. The advantages that allophane enjoys are that it does not require a large pH change to be effective, it is non-toxic, and it is potentially considerably cheaper.

14.7 Applications

It would appear that allophane could be used as a flocculant for the harvesting of algae from oxidation ponds. An approximate estimate of the amount required would be the same weight of algae (oven-dried). Typically systems such as oxidation ponds produce algae at a rate of about 120 kg per 10^6 litres per day.³⁹⁵ The oxidation ponds at Mangere, which treat the sewage of the Auckland metropolitan region, currently process 4×10^8 litres daily.⁴²⁴ This would require about 50 tons of allophane for flocculation each day if ponds were operating at this rate.

A New Zealand lake that is undergoing accelerated eutrophication is Lake Rotorua. This lake is surrounded by extensive deposits of tephra containing allophane. It has been suggested that the enhancement of eutrophication over the last twenty years may be related to the reduction of soil erosion that has been effected in this period. Prior to this there was extensive soil erosion as large areas of the lake's catchment were stripped of their native forests to allow establishment of pastures. During floods, large amounts of allophanic clays derived from the subsoils were washed into the lake and there may have flocculated small organisms containing large quantities of phosphorus, nitrogen and other nutrients. This would bring about their rapid sedimentation and possibly their removal from the nutrient cycle. With the halting of soil erosion this process has been curtailed.

The possibility of adding a flocculant to a lake to remove a large proportion of its microbiological biomass was suggested in the introduction to this chapter. Because of the large volume of water to be treated a plentiful supply of an effective flocculant would be necessary. For Lake Rotorua this is available within its catchment in the form of the clay mineral allophane which may in any case have

once been a natural agent for the removal of nutrients by this method.

The levels of phytoplankton, the organisms in which the greater part of the biomass can be found, fluctuate greatly in this lake throughout the year. Total cell volumes of between 1 and $8 \times 10^3 \text{ m}^3$, with mean annual values of $2.14 \times 10^3 \text{ m}^3$ in 1968 and $2.44 \times 10^3 \text{ m}^3$ in 1969 were determined by Fish.⁴²⁵ Assuming that a one-to-one oven dry weight basis is also suitable for flocculation of this type of suspension, and the flocculation was carried out when the algal concentration was at a maximum, about 10^3 m^3 of allophane, or about $5 \times 10^3 \text{ m}^3$ (8000 tons) of a typical allophanic subsoil, would need to be dispersed through the lake. This amount of soil would be that covering a football field to a depth of about one metre.

CHAPTER FIFTEEN

SUGGESTIONS FOR FURTHER WORK

Interactions of Allophane

To further promote the industrial utilization of allophane and to provide a greater understanding of its reactivity in the natural environment, the interactions of allophane with the following materials should be studied.

Cations. The adsorption of cations by allophanic soils is a phenomenon of considerable economic importance. Thus the adsorption and displacement of agriculturally important cations, in addition to those already studied, from solutions of simple salts, and also from solutions similar to those found in the soil, should be investigated. In particular the influences that different species have upon the adsorption of others should be determined. For example the influences of anions, such as chloride, sulphate and phosphate, upon cation adsorption by allophane are important in agriculture but are not known. A further particular problem that is not understood is the loss of magnesium from allophanic soils that sometimes follows the application of potassium fertilizers.

Anions. The general characteristics that control the adsorption of simple anions by allophane need to be established, again because of their importance in the soil. These reactions should also be correlated with electrochemical models of the allophane surface.

Organic Materials. Very little is known of the interactions of simple organic compounds with allophane. It is possible that an investigation of such interactions would find further properties of allophane that could result in its utilisation in other processes. The scope for study in this field is almost boundless.

The adsorption characteristics of the polymers that form the external surfaces of microorganisms govern the interactions of the organism with other surfaces. Very little is known of the interactions of various polysaccharides and lipids with surfaces like that of allophane. There is also a paucity of knowledge of the influence of such materials upon the colloidal properties of allophane and other minerals.

Viruses. The actual effectiveness of virus deactivation by allophane needs to be established by sensitive analytical procedures such as tissue culturing. Furthermore, the interaction of allophane with pathogenic viruses warrants further study in view of the potential use of allophane for the treatment of sewage. The influence of the presence of other components of effluents upon virus adsorption should also be determined.

Bacteria. Cooper³⁶ has shown that allophane is able to form adsorption complexes with bacteria. However, the factors that influence this interaction are not known. In particular, the optimum conditions at which allophane can remove bacteria from effluent should be established.

Algae. The flocculation of different algal species by allophane should be studied; so too should the rates of flocculation that are found under different conditions. In view of the success that was achieved in the laboratory it is believed that an experimental program⁶⁷ on a much larger scale should be initiated.

The Utilization of the Products from the Interactions of Allophane with some of the above Materials

The properties of the materials obtained after interaction of allophane with the materials referred to above should be investigated to determine their value and possible utilization. For instance, the

algae/allophane floc and the material recovered after the interaction of allophane with proteinaceous wastes are likely to have considerable value as stockfoods. It is probable that where such wastes are not suitable for stockfoods they will have value as fertilizers or soil conditioners.

Other Studies with Allophane

The possibility of using columns of sterilized allophanic soil to produce potable water from water contaminated by microorganisms would be a worthwhile investigation. Such a process could perhaps be incorporated into water recycling within industrial complexes like meat packing plants.

Studies of lake sediments may give further evidence of the manner in which allophane may have been involved in the precipitation of microorganisms from lakes within the volcanic regions of New Zealand. Furthermore experimentation to determine the influence of allophanic clays upon typical waters from eutrophying lakes would assist in determining whether there is any possible benefit to be gained by adding large quantities of this mineral to such lakes. This could be readily done by temporarily increasing erosion.

Further Development of the Proposed Electrochemical Model of Ion Adsorption at the Hydrous Oxide/Aqueous Interface

The stage to which the electrochemical model for ion adsorption at the hydrous oxide/aqueous interface has been developed has provided a sound basis for the interpretation of the cation adsorption interactions of allophane. Its applicability to the adsorption of anions by hydrous oxides and also by allophane needs to be established. Furthermore, to allow its real value to be determined it is necessary that a complete solution to the model is obtained.

CHAPTER SIXTEEN

CONCLUSIONS TO THE STUDY

16.1 Properties of Allophane

The Surface Aluminium

It has previously been proposed that the octahedral aluminium in allophane may be present as a single layer adsorbed onto the aluminosilicate matrix^{25,38,40} or, alternatively, it may be present as discontinuous units of amorphous polymeric aluminium hydroxide.^{37,244} Evidence for the existence of aluminium in both forms has been obtained in this work. This has come from studies of the dissolution of allophane in acid solution, from cation adsorption and from electrophoresis, all coupled with theoretical considerations. For instance it was found that the concentration of aluminium in solutions at equilibrium with suspended allophane was similar to that found with amorphous aluminium hydroxides at the same pH. Furthermore aluminium competed for adsorption sites with other cations which could displace it at high concentrations. Thus the octahedral aluminium found with allophane is distributed between a discrete phase of aluminium hydroxide and monomeric or polymeric hydrolysed aluminium species of low molecular weight occupying cation adsorption sites associated with the aluminosilicate matrix. The position of this distribution is dependent upon the pH of the system. This results from the solubility of the aluminium hydroxide being much more pH dependent than the adsorption of the aluminium ions. There is a slow dissolution of aluminium from the hydroxide with acidification; some of this material re-adsorbs at cation retention sites, displacing less strongly sorbing cations.

Allophane is an aluminosilicate coated to a variable degree with polymeric aluminium hydroxide. This imparts a high isoelectric point to the colloid and sets it apart from the other common clay minerals.

The high affinity of anions for allophane is also associated with this component. Furthermore, it may be the agent that binds together the small irregular aluminosilicate bodies. For example, it was observed that for the three clays most extensively studied in this work the content of labile aluminium hydroxide increased with the mean particle diameter.

The Iron(III) Component

Allophanic clays generally include a significant proportion of an iron(III) material which is probably present as a discrete phase of iron(III) hydrous oxide and not as an adsorbed species. Evidence for this was obtained from the lack of dependence of electrophoretic properties upon its presence, from absorbance spectra of allophane suspensions, and from dissolution studies coupled with theoretical considerations using the proposed electrochemical model.

Because of the similarities of the aqueous surface chemistry of their hydroxides, iron(III) and octahedral aluminium in allophane would behave in complementary manners. In particular, because of its tendency to be positively charged below pH 8, the iron(III) hydrous oxide units would assist in binding together the aluminosilicate bodies. However its importance would be much less than that of aluminium because it is not as widely distributed across the surface; for example, it does not appear to occupy many cation retention sites. It is then predominantly the surface aluminium hydroxide that is responsible for the amphoteric properties of allophane.

The Surface Charge

The remainder of the surface of allophane that is not covered by aluminium in either form, or is associated with the hydrous iron(III) oxides, is exposed amorphous aluminosilicate matrix. This may result

in exposure of weak acid hydroxyl groups or cation retention sites. The surface of allophane is then a combination of different surface groups. Because the reactive groups are hydroxylic, it was possible to determine the surface charge (at least under neutral or alkaline conditions), by potentiometric titration. The variable population of surface groups occupied by aluminium in acidic suspensions and the consumption of acid by aluminium hydroxide dissolution made this method of surface charge determination more complicated at low pH. The point of zero charge found by titration (4.8 for Ohaupo allophane) reflected the contributions made to the surface charge by both the amphoteric aluminium hydroxide (high point of zero charge component) and the weakly acidic hydroxyl groups of the exposed aluminosilicate matrix (low point of zero charge component). Treatment of allophane with reagents able to remove the amphoteric component caused a reduction in the positive component of the surface charge and enhanced the acid nature. If dilute acid was used for this treatment the increased acidity was associated with the adsorption of H^+ in an ionic form. The surface charge of the clay in this form in acid suspension is dependent only upon the pH and, unlike the hydrous oxides to which the behaviour is otherwise analogous, almost independent of the electrolyte concentration. On standing aluminium slowly replaces H^+ from these cation retention sites and the dependence of the surface charge upon the electrolyte concentration returns.

Adsorption of Cations by Allophane

Cations are adsorbed by allophane in response to the development of surface negative charges which may arise from the loss of other cations or by deprotonation reactions. The nett adsorption process is then an ion exchange. The negative charge itself may originate from dissociation of surface groups or from isomorphous replacement within

the aluminosilicate matrix.

The extent to which various cations are bound was found to be dependent upon the same parameters, and in a similar manner, to those that influence cation adsorption by hydrous oxides. In general, for neutral systems, large diffuse cations are bound more strongly than small cations of the same charge. Higher charge cations are also preferred to those of lower valence, as were those that actively hydrolyse. Large differences were found in the dependence of the adsorption upon pH. For instance, little variation was found for the adsorption of the large, diffuse K^+ or Tl^+ ions but binding of Na^+ , Ca^{2+} or Co^{2+} ions increased greatly with pH. This resulted in large changes in the apparent selectivity. For instance, from solutions of the same concentration, Tl^+ was adsorbed to a lesser extent than the divalent cations at pH 5, yet at pH 3 it was preferred to all those that were not partially hydrolysed. Adsorption preference sequences found, for adsorption from 10^{-4} M solution, were at pH 4.0: $Pb^{2+} \gg Tl^+ > Sr^{2+} \sim Co^{2+} \sim K^+ > Ca^{2+} > Na^+$, and at pH 6.0: $Pb^{2+} \gg Sr^{2+} \sim Co^{2+} > Ca^{2+} > Tl^+ > K^+ > Na^+$.

For these cations, at constant total concentration, the distribution between the dissolved and the adsorbed states was a simple function of pH and could be described by simple linear equations. For any system two equations were found; one at high pH and the other at low. These two parts to each isotherm were due to adsorption with and without competition from aluminium and so their point of intersection varied with the concentration and nature of the electrolyte in the solution.

Colloid Properties of Allophane

The isoelectric point of an allophane clay derived from Ohaupo soil was found, by electrophoresis, to be near pH 6 although the exact value was dependent upon the treatment that the clay received.

This value is more than 3 pH units higher than the isoelectric points of the other common clay minerals and most organic colloids. At normal soil pH allophane is one of the few natural colloids that has only a low net charge be it positive or negative. The high isoelectric point also reflects the influence of the surface aluminium present both as its hydroxide and as small cationic species bound by surface cation adsorption sites. The difference observed between the isoelectric point and the point of zero charge may well be due to there being a greater deposition of aluminium hydroxide on the external surfaces of the particles than on the internal surfaces.

The most important mechanism for the coagulation of allophanic suspensions is by adjustment of the pH of the suspension towards the isoelectric point. This can be done by addition of acid or base as necessary, or by the addition of salts, which, by displacing potential determining ions from the surface alters the pH towards the point of zero charge. Multivalent ions are more effective than monovalent ions only when they are surface charge counterions.

Adsorption of Biopolymers by Allophane

The adsorption of charged biopolymers, such as RNA and protein by allophanic clays, has been shown to be similar to their adsorption by other materials although the extent of adsorption is different. The amount of adsorption is in general a property of the surface but the variation with pH is a property of the polymer. In all cases adsorption apparently approached a maximum at pH near the isoelectric point of the polymer and so it was the charge properties of the polymer and not those of the surface, which dominated the interactions. A typical maximum adsorption capacity of allophane for protein is about 10% by weight.

Interactions of Allophane with Viruses

Allophane was shown to remove viruses from suspension very effectively although the real extent to which it accomplished this can be determined only by more sensitive techniques than were available for this study. The interaction was most effective at pH between the isoelectric points of the two colloids; the interaction was a heterocoagulation process. Some evidence that suggested that the viruses may be destroyed upon interaction with the clay surface was found.

An Electrochemical Theory of Ion Adsorption by Hydrous Oxides

At the beginning of this work no theories had been sufficiently well developed to explain convincingly the relationship observed between cation distribution and pH, as observed for allophane in particular. Thus a recent model which describes the interaction of the potential determining ions at the hydrous oxide/aqueous interface was extended to elucidate the adsorption behaviour of the electrolyte. This model assumes that cation adsorption occurs after surface deprotonation and the adsorbed cations lie in a Stern layer at a distance from the surface which is determined by the properties of both the cation and the surface.

The factors that were found to be involved in the adsorption reaction included the following:

the ionic charge and radius,

the amount of surface available for adsorption,

the stability of the adsorption complex,

the ease of dissociation of the surface hydroxyl groups,

the difference in the electric potential experienced by the two exchanging ions in their adsorbed states. In addition, the degree of surface saturation and the presence of competing ions, including those

from the dissolution of slightly soluble hydroxides, all influence ion adsorption in predictable manners.

By using this model to interpret experimental observations from the literature, further evidence that suggested that the surface of precipitated silica is porous was obtained. (It is generally believed that the surfaces of hydroxides and hydrous oxides are discrete.)

This proposed model was able to give a sound electrochemical basis for the observations of the adsorption of cations by allophane and also hydrous oxides. However, at all times the allophane surface appeared to be saturated. For this reason in particular, further development of the model is called for to allow quantitative predictions to be made with greater justification.

Flocculation of Algae by Allophane

There is some circumstantial evidence that lakes and rivers in regions of allophanic soils are less eutrophic than might otherwise be expected. It was therefore of interest to study the interactions of allophane with algae.

It was found that suspensions of *Chlorella vulgaris* were flocculated by small amounts of dispersed allophane. The process proceeded even at a pH where both colloids displayed relatively high negative charges that were sufficient to ensure that each was separately stable in suspension. The mode of interaction, at pH 7 at least, was concluded to be by adsorption of polymers, from the slime layer of the algae, to the clay which then acted as a bridge between adjacent cells. Effective removal of the algae from suspension could be achieved by the addition of about an equal weight of allophane (both on an oven-dry basis).

Comparison of Allophane with other Clay Minerals

Allophane shows some similarities to halloysite and kaolinite. In particular, they are all constant potential materials and they have similar interactions with cations. Removal of surface aluminium from allophane gives it electrophoretic properties like those of halloysite. Furthermore, equilibrium of halloysite in acidic media which has a low electrolyte concentration brings about a transfer of aluminium from the matrix to cation adsorption sites; this gives it electrophoretic properties like those of allophane. Thus allophane is, in many ways, like finely divided halloysite onto which aluminium has been deposited.

The major differences between allophane and halloysite (and hence kaolinite) are:

- (a) the aluminosilicate part of allophane is much less regular and less extensive, and
- (b) in allophane the aluminosilicate part is covered to a variable extent with aluminium hydroxide which is absent in halloysite.

The properties that result from these two structural features, especially the influence of the aluminium hydroxide, set allophane apart from the other common aluminosilicate clay minerals.

16.2 Allophane in the Natural Environment

Allophane is adsorbed by bacteria³⁶ and algae. In this state it will moderate the extent to which many factors, such as pH and the presence of toxins, would influence the growth of the organisms. Furthermore, in suspension this adsorption reaction leads to floc formation, a phenomenon by which microorganisms may be removed from the bodies of lakes.

In the bodies and sediments of lakes and rivers allophane may be active in binding nutrients, especially phosphate, and altering the

rate at which they are recycled.

There is also some circumstantial evidence which suggests that materials like allophane may destroy viruses in rivers.

16.3 Possible Industrial Utilization of Allophane

There are some billions of tons of allophane distributed throughout the central and northern parts of the North Island of New Zealand in a form from which it could be readily retrieved with little environmental damage. One of the principal aims of this work was to investigate whether it could be exploited industrially. It was found that it has potential for use in the following situations.

Flocculation of Algae in Oxidation Ponds

Because of its potential value as a stockfood, and also because of its ability to enhance eutrophication, the algae that grows in oxidation ponds need to be recovered before the water is discharged into waterways. Much of this algae is like *Chlorella* and is amenable to aggregation and precipitation by flocculation. It is suggested that allophane could be used for this process as it is a relatively effective flocculant,⁶ it is cheap and it is non-toxic.

Treatment of Effluents Containing Suspended Colloids

Many effluents from a wide range of industries contain suspended colloidal material. In general these colloids have low isoelectric points, e.g., bacteria, viruses, and much other organic matter that is found in the effluents from sewage treatment plants, pulp and paper mills and food processing industries. It has been shown that allophane interacts strongly with such materials, especially at pH near 5 or lower. This is of course in the pH region where allophane is itself coagulated readily. For most efficient removal of such colloids

allophane would perhaps be most effective as a flocculant, i.e., used to coat particles and reduce their effective surface potentials and also to act as a bridging agent between particles. In this rôle a finely divided allophane with a high external surface and a high isoelectric point would be desired.

Treatment of Effluents Containing Dissolved Inorganic Materials

Soluble inorganic species can be divided into two categories; viz., anions and cations. These are small units and so a large nett surface area would be required for maximum adsorption per unit weight of adsorbent. Although montmorillonite has an extremely high capacity for cations it has only a very low affinity for anions and it is also relatively difficult to remove from suspension except at low pH where its cation adsorption capacity is reduced. However allophane, whilst having a lower capacity for cations, has a high affinity for anions and coagulates rapidly at near neutral and slightly acid pH. It is likely that the combination of these properties would give allophane few rivals amongst the common clay minerals for use in this manner.

From the studies of cation interactions that are reported here it is likely that the pH at which any adsorption process is carried out may have a bearing upon the allophane chosen. For instance, if both cation and anion adsorption were important at pH 5 it is probable that the Ohaupo clay would be the more suitable whilst at pH 7 Tirau clay may be more effective.

Treatment of Effluents Containing Dissolved Organic Materials

Soluble organic materials are found in many effluents. They are often the cause of the discolouration of many waters, they usually enhance eutrophication and, in many cases, they have some commercial

value. It has been shown in this study that the removal of ionisable polymeric organic compounds can be achieved by allophane from solutions near pH 5 although the optimum pH for maximum removal is dependent upon the polymer. The use of allophane as an adsorbent for the treatment of wastes from such industries as pulp and paper mills, sewage treatment plants and food processing factories is suggested. In laboratory scale experiments significant improvements in the quality of slaughterhouse effluents, including an almost complete removal of colour, has been achieved.¹⁵⁷ It is believed that the potential for the utilization of allophane for the treatment of such wastes is considerable and large scale operations should be attempted.

Thus it can be seen that allophane shows exciting prospects for utilization as a commercial product.

APPENDICES

Appendix I STATUS "Polyfit" Program

A STATUS* program was used to obtain a least squares fit polynomial of the form $y = \sum_n a_n x^n$ for the volume of the suspension added to the centrifuge and the weight of centrifugate obtained (see section 3.7, Particle Size Studies). The program was run on an IBM 1130 computer and a typical printout is reproduced overleaf.

In operation the program was entered into the computer from punched cards. The data for each parameter were entered as $1 \times n'$ matrices where n' was the number of data points. The power coefficients were specified in the matrix POWS. Polynomials for any number of sets of data could be obtained by having the data cards for each matrix in order after the load statement for that matrix when it had been specified that it would be repeated.

The program output gave a program listing, the two input matrices, the least squares coefficients, a plot of the deviation of the experimental points from the polynomial function and the power matrix. The polynomial function used for further computation was that which had the least skew in the plot.

* Statistical Computing, Ultra-Simple; a simple matrix-handling language base on SMIS but greatly extended and simplified by W.J. Rogers and J.C. Turner, Department of Mathematics, University of Waikato.

MATRIX INTERPRETIVE PROGRAM - SMIS

POLYFIT PROGRAM

```

1      REMK 5
7      LOAD X (REP)
13     LOAD Y (REP)
19     LOAD POWS 1 4
21     LPTO 5
22     PRNT X 1
24     PRNT Y 1
26     POWV X POWS 0
27     TRNS 0 DTR
28     MULT DTR 0 LHS
29     DUPL LHS LHSI
30     INVT LHSI
31     MULT DTR Y REST
32     MULT LHSI REST A
33     PRNT A 1
35     MULT 0 A NEWY
36     SUB NEWY Y NEWY
37     S PLOT X NEWY
38     PRNT POWS

```

LEAST SQUARES POLYNOMIAL
 PARTICLE SIZE ANALYSIS BY CENTRIFUGATION
 CONDITIONS: 250FG C. 1200RPM, 900SEC
 CLAYS
 MANGAWARA

VOLUME

MATRIX X(1)

```

1      0.00000
2      2.00000
3      2.00000
4      4.00000
5      4.00000
6      6.00000
7      6.00000
8      8.00000
9      8.00000
10     10.00000
11     10.00000
12     12.00000
13     12.00000
14     12.00000
15     12.00000
16     14.00000
17     14.00000
18     16.00000
19     16.00000
20     20.00000
21     20.00000
22     22.00000
23     22.00000

```

WEIGHT

MATRIX

Y(1)

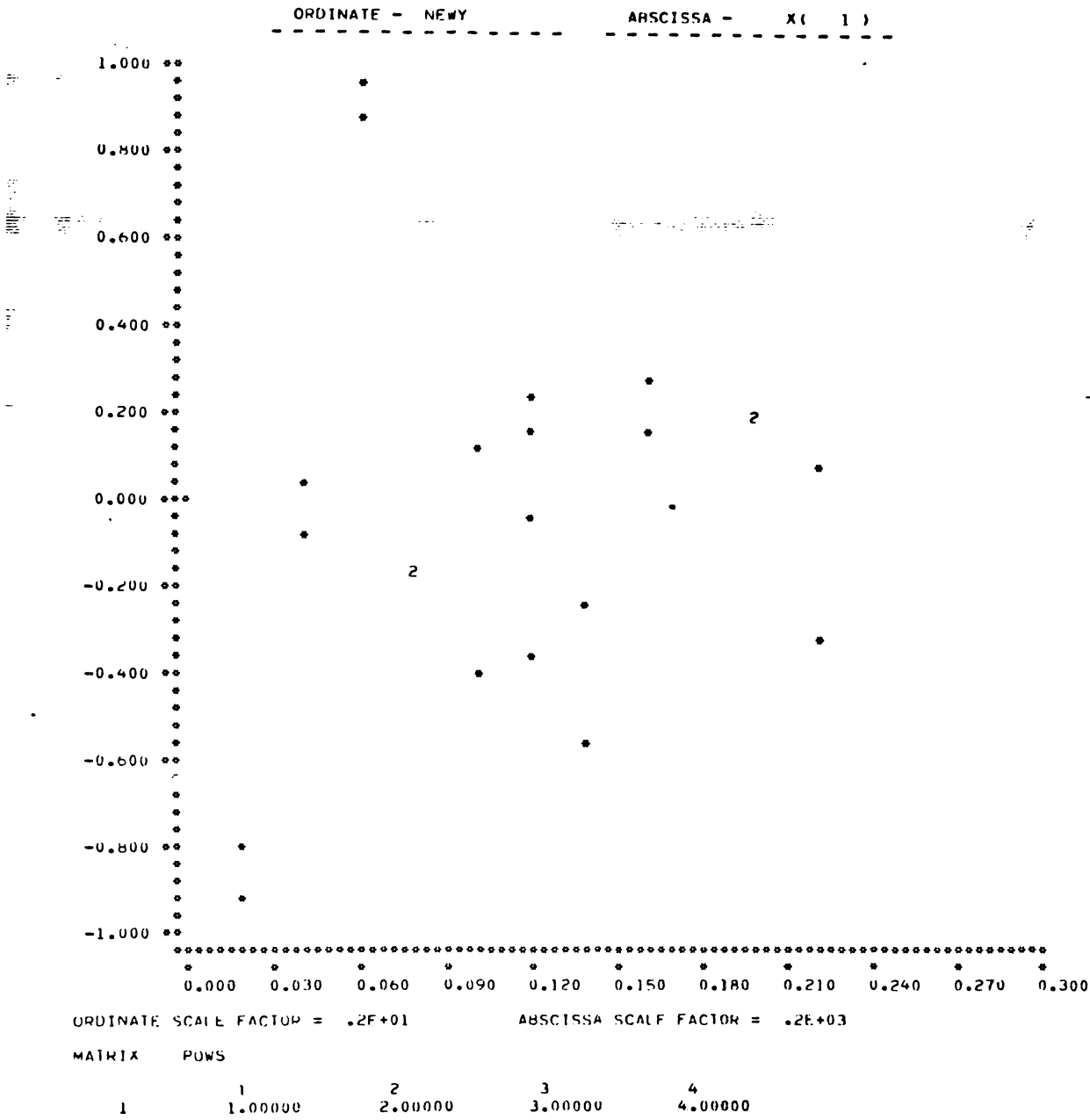
	1
1	0.00000
2	7.80000
3	7.70000
4	11.60000
5	11.70000
6	14.00000
7	13.90000
8	17.40000
9	17.40000
10	19.00000
11	19.50000
12	20.60000
13	21.20000
14	20.70000
15	20.90000
16	23.20000
17	22.90000
18	24.40000
19	24.30000
20	28.20000
21	28.20000
22	29.80000
23	30.20000

LEAST SQUARES COEFFICIENTS

MATRIX

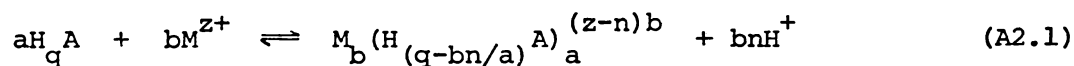
A

	1
1	4.12404
2	-0.37292
3	0.01843
4	-0.00033



Appendix II The Inadequacy of Kolarik's Model for
Cation Adsorption by Hydrous Oxides

Kolarik²⁶⁵ proposed that the adsorption of cations by hydrous oxides (see section 7.2.1) could proceed by the following process:



The major difference between this mechanism and that of Kurbatov et al.²⁶³ is the provision for more than one cation to adsorb at any site. The equilibrium constant, K_{ab} , for this process, from mass action considerations and replacing activities with concentrations, was given by;

$$K_{ab} = \frac{\frac{1}{a} (N_o - [H_qA])[H^+]^{bn}}{[H_qA][M^{z+}]^b} \quad (A2.2)$$

where N_o is the total number of surface adsorption sites. The distribution coefficient for the cation M^{z+} is given by;

$$D = (N_o - [H_qA])/[M^{z+}] \quad (A2.3)$$

and so from (A2.2) and (A2.3);

$$\log D = \log aK_{ab} + (b - 1)\log[M^{z+}] + \log[H_qA] + bn \text{ pH} \quad (A2.4)$$

Differentiating (A2.4) with respect to pH yields;

$$\frac{d \log D}{d \text{ pH}} = (b - 1) \frac{d \log[M^{z+}]}{d \text{ pH}} + \frac{d \log[H_qA]}{d \text{ pH}} \quad (A2.5)$$

For low concentrations of the adsorbing cation Kolarik put $b = 1$. The situation then was the same as that described in section 7.3.1,

and the slope of the plot of $\log D$ against pH was n .

For higher cation concentration Kolarik put $b > 1$. In this case for less than saturating amounts of the cation when $\log d < 0$ then $\log [M^{z+}]$ was constant, but when $\log D > 0$ then $\log [M^{z+}]$ will vary greatly with pH . Thus $d \log D / d pH$ will change value at $\log D = 0$. This was not observed by Kolarik or by any other worker. The model proposed by Kolarik must be considered inadequate.

Appendix III The Relationship between Equation (7.26)
 and the Stern Equation (4.28)

The following relationship was developed in section 7.3.1 to describe the distribution of surface sites of a hydrous oxide, HA, in contact with an aqueous solution of a monovalent salt, MX,

$$N_o = [AM] \left[1 + \frac{1}{\Omega_m} + \frac{\Omega_-}{\Omega_m} + \frac{\Omega_-}{\Omega_m \Omega_+} + \frac{\Omega_- \Omega_x}{\Omega_m \Omega_+} \right] \quad (7.26)$$

For cation adsorption the last two terms of (7.26) can usually be ignored as they represent cation adsorption in conditions where it is not favoured (very low pH). The concentration of cations in the inner Helmholtz Plane (IHP) is given by;

$$[AM] = N_o / \left[1 + \frac{1}{\Omega_m} + \frac{\Omega_-}{\Omega_m} \right] \quad (A3.1)$$

Similarly for anion adsorption it can be shown that;

$$[H_2AX] = N_o / \left[1 + \frac{1}{\Omega_x} + \frac{\Omega_+}{\Omega_x} \right] \quad (A3.2)$$

The total charge in the IHP, σ_β , is given by the sum of the components;

$$\begin{aligned} \sigma_\beta &= ([AM] - [H_2AX]) / A_v \\ &= \frac{N_o / A_v}{1 + \frac{1}{\Omega_m} + \frac{\Omega_-}{\Omega_m}} - \frac{N_o / A_v}{1 + \frac{1}{\Omega_x} + \frac{\Omega_-}{\Omega_x}} \end{aligned} \quad (A3.3)$$

$N_o / A_v = N_1$, the total surface concentration possible adsorption

sites. Rearranging (A3.3) gives;

$$\sigma_{\beta} = \frac{N_1 \Omega_m}{1 + \Omega_m + \Omega_-} - \frac{N_1 \Omega_x}{1 + \Omega_x + \Omega_x} \quad (\text{A3.4})$$

Incorporating (7.18) to (7.21) into (A3.4) gives;

$$\begin{aligned} \sigma_{\beta} = & \frac{N_1 [M^+] \exp(-\frac{e}{kT} \psi_{\beta m}) / K_m}{1 + [M^+] \exp(-\frac{e}{kT} \psi_{\beta m}) / K_m + [H^+] \exp(-\frac{e}{kT} \psi_o) / K_-} \\ & - \frac{N_1 [X^-] \exp(\frac{e}{kT} \psi_{\beta x}) / K_x}{1 + [X^-] \exp(\frac{e}{kT} \psi_{\beta x}) / K_x + K_+ \exp(\frac{e}{kT} \psi_o) / [H^+]} \end{aligned} \quad (\text{A3.5})$$

This equation represents the charge in the Stern layer for both completely reversible and polarisable double layers.

For the completely reversible double layer, e.g., the hydrous oxide/aqueous interface, the third term in each denominator indicates the dependence of the surface charge upon the concentration of the potential determining ions (in this case H^+ and OH^-). The second term in the denominator is shown in section 7.3.1 to be unimportant for hydrous oxides as it represents the situation when the surface is in a highly ionised situation with little adsorbed electrolyte. In such a case there would be a large diffuse layer charge and this is not generally found.²⁶⁷

For the completely polarised double layer, e.g., the mercury/aqueous interface, there are no potential determining ions and the third term in each denominator of (A3.5) can be neglected. (A3.5) then has the form of the Stern equation as given by Overbeek⁸⁴ (his equation (55)) or (4.28) of Chapter Four. The specific adsorption potentials, ϕ^+ and ϕ^- of (4.28) can be identified with K_m and K_x of (A3.5) respectively. Ideally for such a surface in contact with an aqueous solution terms relating to the concentration of all ionic

species in the IHP, including H^+ and OH^- should be included in (A3.3).

Appendix IV Problems of Determining the Adsorption of
Strontium and Calcium by Allophane at low pH:
Interference of Aluminium in the Determination
of Calcium and Strontium by Flame Emission and
Atomic Adsorption

During analysis of solutions from suspensions of clays equilibrated at reduced pH in dilute solutions of strontium or calcium in 10^{-3} M sodium chloride there appeared to be an anomalous reduction in the concentration of the divalent cation. It was suspected that this interference, which persisted in the presence of 1% potassium chloride, might be due to the aluminium that had dissolved from the allophane although this problem does not seem to be reported in the literature. To verify this supposition a number of solutions of various composition were prepared and analysed for both strontium and calcium, both by flame emission (FE) and calcium also by atomic adsorption (AA). The solutions which contained aluminium were also treated with oxine solution (8-hydroxyquinoline) which precipitates aluminium and iron(III) in the following manner: 5 ml of solution was mixed with 1 ml of oxine solution (5.0 g oxine and 10 ml glacial acetic acid made up to 100 ml with distilled water and then filtered) and 1 ml of 10% ammonium acetate at pH 5.5. The mixture was then heated to 70 to 80°C in a water bath, cooled and centrifuged to deposit the precipitate. The solution was then analysed by flame emission or atomic adsorption as required with a Varian-Tectron atomic adsorption spectrophotometer. Other samples of the same solutions had sufficient lanthanum nitrate added to them to make them 0.2% in lanthanum. The possibility of interference by hydrochloric acid and traces of iron(III) was also investigated. The results of these

experiments are displayed in Table A.1 which lists the depression of the spectrophotometer meter reading for each sample.

The depressive effect of aluminium on strontium and calcium in the AA and FE determinations was notable for aluminium concentrations greater than 10^{-3} M (30 ppm). This interference could be masked by the addition of lanthanum although this had a tendency to enhance the signal to a small extent. The oxine treatment was more troublesome but it was more reliable. Strong acid (0.1 M HCl) also had a depressive effect but addition of a quantity of near neutral buffer reduced this effect. Iron(III) in the concentrations commonly found in this study (see section 8.3.2) did not appear to influence the determination of calcium or strontium.

For all routine analyses of strontium and calcium both potassium chloride (1%) and lanthanum nitrate (0.2%) were added to solutions of pH greater than 3.0. Low pH extractants were treated with oxine solutions. The standard solutions used were subjected to identical treatment.

Table A.1 Interferences in the Determination of Strontium and Calcium by AA and FE

Solution composition				percent depression					
[Sr]	[Ca]	[Al]	[Fe]	Strontium			Calcium		Calcium
				soln	FE oxine	La	soln	FE oxine	AA soln
10 ⁻⁴ M									
1	1	-	-	0	0	0	0	0	0
1	-	-	-	0	-	-	-	-	-
-	1	-	-	-	-	-	0	-	-
2	1	-	-	-	-	-	0	-	-
1	1	0.4	-	0	0	-	0	-2	0
1	1	1	-	-1	0	-	-2	-2	-3
1	1	4	-	-1	0	2	-2	-4	-5
1	1	10	-	0	-1	0	-4	0	-5
1	1	40	-	26	-1	-1	43	0	24
1	1	100	-	26	0	-1	41	-4	15
1	1	-	0.2	0	-	-	0	-	-
1	1	-	0.5	-1	-	-	0	-	-
1	1	-	2	0	-	-	0	-	-
1	HCl	pH 3		0	-	-	-	-	-
1	HCl	0.1 M		6	-	-	-	-	-

Appendix V Composition of Algal Growth Media

The nutrient mixture used for growing algal cultures was suggested by Dr. E.G. Bollard.* It was prepared by adding together the following solutions and making up to one litre with distilled water.

4 ml	1 M KNO_3
2 ml	1 M MgSO_4
2 ml	1 M $\text{Ca}(\text{NO}_3)_2$
5 ml	0.2 M KH_2PO_4
0.6 ml	FeNa EDTA [†]
1 ml	Trace elements ^{††}

[†]FeNa EDTA: 15 g Na_2EDTA plus 12.5 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 500 ml distilled water, aerated for 24 hours.

^{††}Trace elements: 2.86 g H_3BO_3
 1.79 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$
 0.10 g ZnCl_2
 0.08 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 0.04 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$
 all in one litre of distilled water.

The algal growth medium used was prepared from the nutrient mixture with 5 g glucose added per litre to assist rapid growth.

The algal nutrient agar was prepared by dissolving 18 g Difco Bacto-Agar in one litre of algal nutrient medium.

*Plant Diseases Division, D.S.I.R., Auckland.

Appendix VI Size Properties of *Chlorella vulgaris*

The algal particle size distribution was determined using a calibrated Olympus E-type binocular microscope with 40x objective and 15x eyepiece magnification. The diameter of any cell which passed between the calibration lines as the slide was moved from side to side was recorded to $\pm 0.5 \mu\text{m}$. Several scans were made and over 200 cells measured. Two samples were observed in this manner; the first was actively growing algae and the second was from the same suspension after preparation for sedimentation and flocculation experiments, i.e., after 4 washings with distilled water and standing for 12 minutes per cm depth. The two distributions are shown in figure A.1.

The mean number diameter, D_n , is given by the formula;

$$D_n = \frac{\sum_i n_i D_i}{\sum_i n_i} \quad (\text{A6.1})$$

where n_i is the number of particles in the i th size range, i.e., those particles with diameter $D_i \pm 0.5 \mu\text{m}$.

For the prepared sample $D_n = 7.8 \mu\text{m}$. It is notable that in this sample there was an increase in the proportion of smaller cells due to a loss of the larger bodies which sedimented much more rapidly. The first peak at $5 \mu\text{m}$ corresponded to the juvenile cells which had a diameter of not less than $5 \mu\text{m}$ when their parental cluster disintegrated. The second peak at about $12 \mu\text{m}$ was due to adult clusters of four of the juvenile cells, the product of two consecutive binary fissions. Lin et al.⁴⁰⁸ gave the size range for cells taken

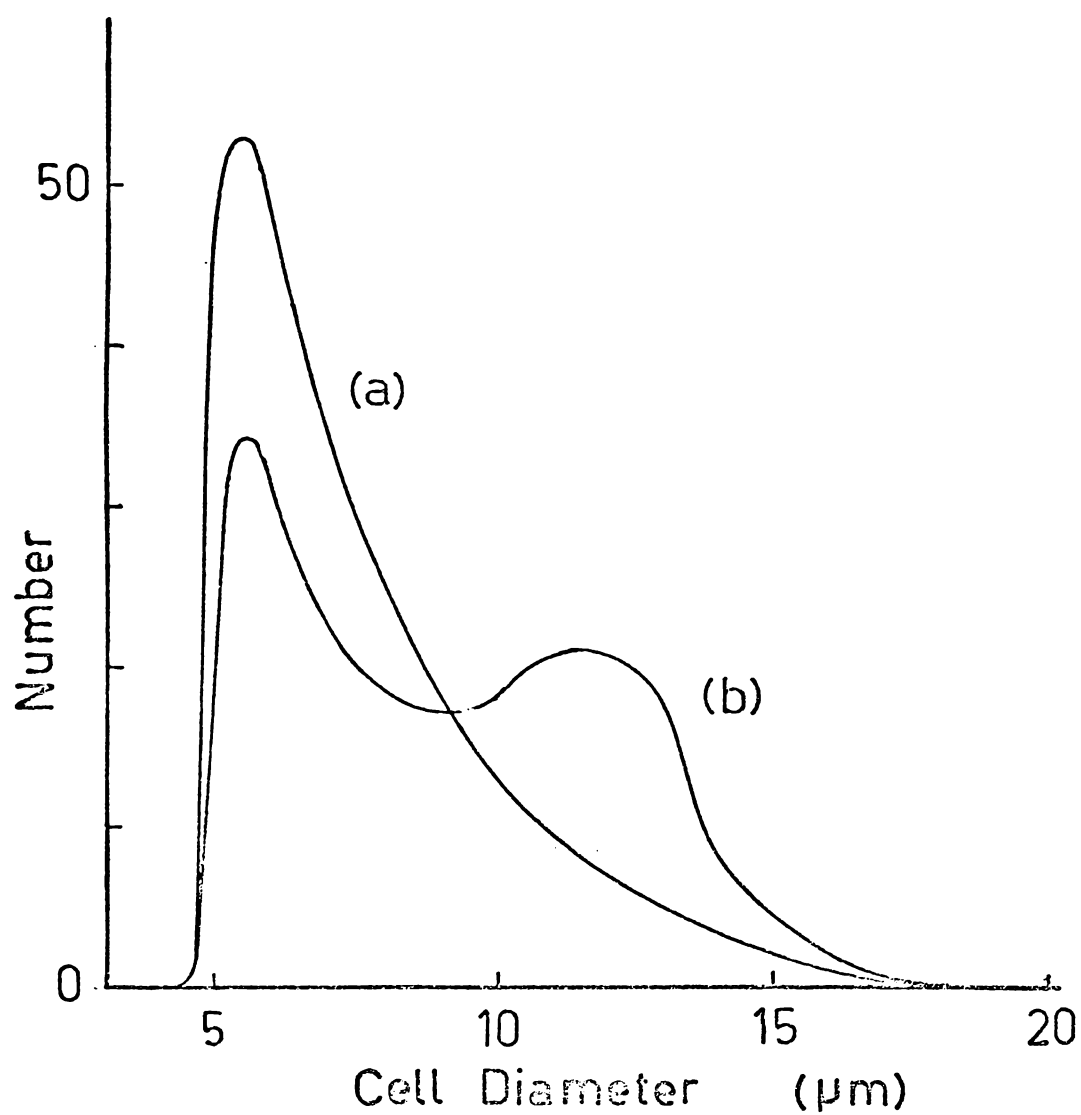


Figure A1. Size distribution of the cells of *Clorella vulgaris* samples (a) as used for experiments and (b) freshly grown.

from a river as 1.5 to 10 μm diameter. The growing conditions in the laboratory were apparently more invigorating than in unprotected, competitive natural systems.

The mean volume diameter, D_v , the diameter of the cells of mean volume or weight, is given by;

$$D_v^3 = \frac{\sum_i n_i D_i^3}{\sum_i n_i} \quad (\text{A6.2})$$

For the sample prepared for experimentation $D_v = 8.0 \mu\text{m}$. The mean volume was then about $270 \mu\text{m}^3$.

A sample containing 3×10^9 cells was collected on a pre-dried and weighed Millipore filter ($0.45 \mu\text{m}$), washed with water and dried at 105°C . The nett dry matter per cell was found to be 1.8×10^{-11} g. This represents about 6.5% dry matter.

Appendix VII Glossary

1. Abbreviations

AA	atomic absorption.
AEC	anion exchange capacity.
BET	Brunauer, Emmett and Teller theory.
c.c.c	critical coagulation ^{concentration} coagulation .
CEC	cation exchange capacity.
DNA	deoxyribonucleic acid.
DTA	differential thermal analysis.
em	electrophoretic mobility.
esd	equivalent spherical diameter.
FE	flame emission.
IEP	isoelectric point.
IHP	inner Helmholtz plane.
OD	optical density.
OHP	outer Helmholtz plane.
p.d.	potential determining.
PZC	point of zero charge.
RNA	ribonucleic acid.
SEM	scanning electron micrograph.
TEM	transmission electron micrograph.
TGA	thermal gravimetric analysis.
TYMV	turnip yellow mosaic virus.
XRF	x-ray fluorescence analysis.

2. Symbols

- a activity, constant, BET slope, reaction stoichiometry coefficient.
- b constant, BET intercept, reaction stoichiometry coefficient.
- c constant, concentration; c_i , concentration in Stern layer; c_s , concentration in bulk solution.
- d distance from surface to OHP, differential operator.
- e electron charge, 2.7183.
- $f()$, $fn()$, function.
- g gravitational acceleration constant.
- i running index = 1, 2, 3 etc., indicates i th species.
- j running index = 1, 2, 3 etc., indicates j th species.
- k optical constant, Boltzman constant; k' , rate constant; k'_0 , rate constant for $V_T = 0$.
- l optical pathlength.
- m constant, mass.
- n number, number concentration, reaction stoichiometry coefficient; n_{app} , slope of experimental log D vs pH plot.
- p partial pressure, $- \log 10$; p_0 , saturation vapour pressure.
- q reaction stoichiometry coefficient.
- r correlation coefficient, radius, radial distance; r_i , radius of particle type i ; r_0 particle radius, radius of curvature of surface; r_w , radius of water molecule.
- t time.
- u distance parameter.
- v velocity; v_t , terminal velocity.
- w constant of proportionality.
- x aliquot volume, distance, concentration, surface concentration (Langmuir and BET), distance, distance from surface, coordinate; x_{max} , surface concentration forming a monolayer.
- y coordinate.
- z ion charge, coordinate.

2. Symbols (continued)

- A absorbance; A_o , surface area per unit weight; A_v , surface area per unit suspension volume.
- D Distribution coefficient, diffusion coefficient, diameter; D_{EM} , Esin-Markov coefficient; D_{ij} , mutual diffusion coefficient of species i and j ; ${}^{ij}D_n$, mean number diameter; D_v , mean volume diameter.
- E extinction, exponential function; E_o , E_d^i , $E^{\pm}$, exponential functions; E_1 , electric field, adsorption energy of first layer; E_L , heat of liquefaction.
- F Faraday constant; F_a , mass related force; F_R , frictional resistance.
- G Gibbs free energy; G_{solv} , Gibbs free energy of solvation.
- H_o distance between surfaces.
- I total ionic concentration, collision frequency, intensity of transmitted radiation; I_a , intensity of adsorbed radiation; I_o , intensity of incident radiation; I_s , intensity of scattered radiation.
- J collision frequency.
- K constant, equilibrium constant; K_a , acid dissociation constant; K_i , K_o , equilibrium constants; K_{so} , solubility product, K_1 , stability constant; K_2^1 , selectivity constant.
- M general representation of a metal cation; M_h , molecular weight of water.
- N Avogadro's number, number concentration; N_1 , surface concentration of p.d. ion adsorption sites; N_o , number of adsorption sites, number concentration at $t = 0$.
- R centrifuge parameter, gas constant, R_{ij} , effective collision radius of particles i and j .
- S centrifuge parameter, reduced distance.
- T temperature (absolute), tube diameter.
- V particle volume, aliquot volume; V_A , attractive interaction energy; V_C , Coulombic interaction energy; V_C^o , Coulombic interaction energy at constant surface charge; V_C^{ψ} , Coulombic interaction energy at constant surface potential; V_{max} , potential energy barrier of particle interaction.
- W stability ratio, weight; W_T , overall stability ratio; W_{ij} , stability ratio for interaction of colloids i and j .
- X change in amount of acid or base, general representation of an anion.
- Y change in amount of dissolved metal species.

2. Symbols (continued)

α	adsorption intensity.
β	distance from surface of adsorbed species at IHP.
γ	distance between IHP and OHP.
ϵ	extinction coefficient, dielectric constant; ϵ_1 , ϵ_m , dielectric constant within IHP; ϵ_2 , dielectric constant between IHP and OHP.
ζ	zeta potential.
η	fluid viscosity.
κ	Debye parameter; $1/\kappa$, double layer thickness.
λ	wavelength, constant.
μ	chemical potential; μ° , standard chemical potential; $\bar{\mu}_i$, electrochemical potential of species i.
v_e	velocity induced by electric field.
π	3.1416.
ρ	density, charge density.
σ	charge density in a plane; σ_o , surface charge density; σ_i , Stern layer charge density; σ_β , charge density of IHP; σ_d , diffuse layer charge density.
τ	turbidity.
ϕ	Galvani potential; $\phi^\pm$, specific adsorption potential; $\phi_o^\pm$, specific adsorption potential of p.d. ions; ϕ_β , self atmosphere potential.
χ	a surface potential.
ψ	electric potential difference, Volta potential; ψ_o , surface potential; ψ_β , potential at IHP; ψ_d , potential at OHP; ψ_o , effective surface potential; ψ_{o1} , effective surface potential of species 1.
ω	radial velocity.
Γ	specific surface excess.
Σ	summation operator.
Ω_i	exponential function.
∇^2	Laplacian operator.

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