CHLORIDE EXCLUSION BY CLAY MINERAL SURFACES

A Thesis submitted

by

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LIST OF SYMBOLS

A	Hamaker constant.
A	measured chloride exclusion areas per g. of clay.
A_o	maximum available surface area per g. of clay.
B'	constant $= \sqrt{\frac{\varepsilon kT}{2\pi}}$
C, C_o	bulk concentration of solute (meq./ml.)
C^+	local concentration of cations at any point in the double layer.
C^-	local concentration of anions at any point in the double layer.
C_I	concentration of potential determining ions.
D	half distance of separation between two opposed plates.
d	distance from charged surface.
E	exchange capacity.
$E\ (k,\varphi)$	elliptic integral of first kind (Jahnke and Emde, 1945).
E_A	electrostatic energy of attraction.
e	electronic charge.
F	Faraday charge
$F(k,\varphi)$	elliptic integral of the second kind (Jahnke and Emde, 1945).
G	free energy of double layer formation per cm^2 surface.
G_o	free energy of diffuse layer formation on area A_o with full charge density σ operative.
G_s	free energy of diffuse layer formation on charged areas A.
k	Boltzmann constant
k	association constant for ion binding.

M	molecular weight of solvent
N	negative adsorption in meq./g. clay.
N	Avogadro's Number.
N_s	number of adsorption sites per cm^2 surface.
n_i	concentration (ions/ml) of ions of kind i at point where the amount of work involved is W_i
n_{io}	bulk solution concentrations (ions/ml).
P	force acting between two plates per cm^2 surface.
p	ratio cationic to anionic valency.
p_o	van't Hoff pressure at outer surface of film.
q	$= -ze\Psi/2kT$.
r	= ionic radius.
R	gas constant.
S^-	number of anions per cm^2 surface.
T	temperature (in degrees Kelvin).
U	$= ze\Psi_d/kT$.
V_m	potential in medium of dielectric constant ϵ_m.
V_w	potential in medium of dielectric constant ϵ_w.
W	volume of water per unit weight of clay from which exclusion is taking place.
X	film thickness.
X_{max}	film thickness on surface of infinitely high charge density.
Y	$= ze\Psi/kT$.
Z	$= ze\Psi_o/kT$.
z	valency

α	fraction of sites at which an ion is bound.
α_-	fraction of particle charge on a single charged surface compensated by a deficit of co-ions.
α'_-	co-ion exclusion fraction for interacting plates.
β	$= \frac{8\pi F^2}{\varepsilon RT}$ where all symbols have their usual physicochemical significance.
Γ	surface charge density
Γ_+	positive adsorption of cations per unit surface.
Γ_-	negative adsorption of anions per unit surface.
Δ	plate thickness.
δ	distance behind charged surface at which extrapolated concentration-distance function of anions reaches zero.
ϵ	dielectric constant.
ϵ_w	dielectric constant of water, bulk solution.
ϵ_m	dielectric constant in adsorbed layer.
φ	specific adsorption potential of counter ion adsorbed to the wall.
θ	$= A_o - A/A_o$
K<	reciprocal of radius of ionic atmosphere.
ρ	space charge density.
σ	surface charge density.
σ_1	charge in the adsorbed Stern layer.
σ_2	charge in diffuse part of the double layer.
$\sigma(r)$	charge distribution function in discrete site model.
ψ	electrostatic potential.
ψ_o	electrostatic potential at the surface.
ψ_1	electric potential in monolayer.
ψ_d	mid-plane potential.

SUMMARY

A study has been made of the repulsion of chloride ions by clay surfaces. The results have been expressed as a volume of water at the clay-solution interface from which chloride is excluded. In the Schofield treatment of negative adsorption, this volume represents $\frac{\Gamma_-}{C_o} . A$ where Γ_- is the chloride repulsion in meq./cm^2 of surface, C_o is the normality of the solution in which the clay is immersed and A is the area of the clay-solution interface. When the volume is plotted against a "depth function" $\frac{q}{\sqrt{z\beta C_o}}$, which may be identified with the Debye-Hückel 2/K, a straight line should be obtained which should be the area of the clay material. The following materials saturated with a series of monovalent (Li, Na, K, NH_4, Rb, Cs), divalent (Mg, Ca, Sr, Ba) and trivalent (Al) ions have been used in the experiments:- Fithian illite (not interstratified), Grundite illite (interstratified), Wyoming bentonite, Milford saponite and a sample of silica.

When the Fithian illite results for the monovalent ions were plotted according to the Schofield equation, a series of straight lines was obtained. The surface areas calculated from the slope of the lines ranged from 80 m^2/g. for the Li-clay to zero for the Cs-clay. The observed areas decrease in the order of ion hydration. The surface area for this mica-like material was measured as about 110 m^2/g. by nitrogen adsorption.

The straight line plots are inconsistent with a reduced charge density smeared out over the whole surface. The results have been satisfactorily analysed in terms of independent sites of localized charge. The number of charged sites depends upon the extent of cation association (immobilization) with the clay surface. As association increases in the series from Li to Cs, the number of free charged sites decreases and hence the measured surface area decreases. However, a straight line relation is still obtained for a given cation because the number of cations associated with the surfaces increases linearly with decreasing concentration. There is a compensation between the number of charged sites and the area of surface pertaining to a dissociated (free) site. This area is $(2/K)^2$.

The proposed model for the double layer on a clay mineral surface involving immobilized ions has been analysed in terms of ion binding (immobility) either at the surface in the primary water layer (inner Helmholtz plane - Fuoss ion pair) or one water layer removed from the surface (outer Helmholtz plane - Bjerrum ion pair).

A generalised equation involving the nett energy of an ion has been derived by considering the electrostatic force of attraction between the oppositely charged ion and surface, and the image energy of repulsion. The latter depends on the difference in dielectric constant between the bulk solution and the adsorbed water layer. An important factor determining ion association is the charge density of the clay surface.

The results for the divalent Fithian illites indicated virtually complete binding for these ions. Thus, no diffuse double layers were formed.

Essentially similar results to those for Fithian illite were obtained for montmorillonite and saponite, except that the degree of association was less. For expanding lattice minerals association on internal crystal surfaces is enhanced by the presence of an opposed plate.

PREFACE

The work presented in this thesis was conducted in the Department of Agricultural Chemistry, University of Adelaide, under the supervision of Dr. J. P. Quirk and Dr. A. M. Posner, Reader and Senior Lecturer in Soil Science respectively.

The thesis contains no material which has been accepted for the award of any other degree or diploma in any University, and to the best of the author's knowledge and belief, the thesis contains no material previously published or written by another person, except when due reference is made in the text of the thesis.

D. G. Edwards
May, 1964.

INTRODUCTION

Many of the characteristics of soils are closely dependent upon the amount, nature and properties of the clay mineral fraction. Because of its large specific surface area, the clay fraction is important in determining the physicochemical reactions involving the adsorption of exchangeable ions and also water.

A large number of practical problems in agriculture and soil mechanics may be better understood when more is known of the fundamental relationships between water, ions and clay mineral surfaces. Ions at the clay-solution interface can profoundly influence such related properties as swelling, water retention and permeability.

As a result of detailed swelling measurements on clay-water systems, Aylmore and Quirk (1960) concluded that the structural status of clay-water systems could only be satisfactorily resolved when water directly associated with the clay surfaces could be distinguished from water which is simply retained by surface tension forces in the pores of a gel structure. Detailed studies of chloride exclusion from particle surfaces in clay-water systems appeared to be an appropriate way of separating surface water from water enmeshed within a gel structure. This distinction is especially important because the pores containing enmeshed water are extremely significant for the transport of ions and water in clays and soils. Posner and Quirk (1964) have recently reported on chloride exclusion from clay surfaces in concentrated electrolyte solutions, and demonstrated the important effects of different exchangeable cations in the surface regions. However, information is required for more dilute solutions, in which diffuse double layers may develop.

The diffuse double layer theory of Gouy and Chapman has proved to be a very useful background for interpreting many experimental measurements in the field of clay-water interaction. However, this theory would seem to be limited in applicability, because it does not take into account differences between ions of the same valency, nor the presence of strong electrostatic attractive forces. In this regard, it is considered that a critical consideration of the electrostatic theories of ion binding on polyelectrolytes may help unravel the problem of the distribution of the exchangeable cations. In fact, it seems logical to treat the large negatively charged, plate-shaped clay mineral particles as macromolecules.

Because clay surfaces are negatively charged there is a deficit of anions near the surfaces. This deficit can be measured as a volume from which chloride or any other anion is totally excluded. This measurement of chloride exclusion may also be regarded as an adsorption or surface excess of water relative to the salt solution within which the clay particles are immersed. It is therefore appropriate that chloride exclusion should be related to the extent of the interface involved.

In this thesis, the phenomenon of chloride exclusion by some common clay minerals has been studied, particularly in relation to the exchangeable cations. This investigation was directed towards understanding the role played by cations of the same valency in different clay mineral-water systems, and consequent differences (if any) in the overall formation of diffuse double layers in these systems. Monovalent, divalent and trivalent (aluminium) systems were studied.

The thesis is divided into four sections. Section 1 contains a review of the relevant literature. Only those equations essential to the development of the main theme have been included. In Section 2, the experimental materials and methods are described. The general results and discussion are presented in Section 3, together with an analysis in terms of ion binding on discrete charged sites. A general theoretical equation of binding is also developed. In Section 4, the general conclusions are summarized and discussed, and some recommendations for future research are made.

1. REVIEW OF LITERATURE

I. DISTRIBUTION OF IONS IN THE VICINITY OF CHARGED SURFACES.

A. Introduction.

Since Helmholtz (1879) first considered the structure of the interfacial region near a charged solid surface, the distribution of ions balancing the charge on the surface has attracted much attention, both theoretical and experimental. Helmholtz's original suggestion that ions were fixed in a layer immediately adjacent to a charged surface was found to be inadequate because it did not take into account thermal motion which allows the ions to move some distance from the charged interface. However the Helmholtz theory will be apposite at absolute zero temperature, where the ions are devoid of thermal energy.

Gouy (1910) recognized that because ions possess thermal energy, there must be a volume density of electric charge in the dispersion medium; the charge is greatest adjacent to the solid phase boundary, and diminishes with increasing distance from the surface. Chapman (1913) independently treated the diffuse double layer at a plane interface. The Gouy-Chapman double layer theory is essentially similar to that derived by Debye and Hückel (1923, 1924) to describe the ionic atmosphere around a spherical, impenetrable ion. They considered this distribution under the opposing influences of the Coulomb forces tending to form an ordered arrangement and the thermal forces tending to give a purely random distribution. The extent of the ionic atmosphere $^1/K$ was shown to be given by

$$^1/K \simeq \frac{1}{3 \times 10^7 z \sqrt{c}} \quad \ldots\ldots\ldots \quad (1)$$

where Z = valency

c = bulk concentration of solute (meq./ml.)

The extent of the ionic atmosphere in the Debye-Hückel theory of strong electrolytes $^1/K$, will later be identified with the thickness of the diffuse double layer formed on a charged, planar surface.

B. Resumé of Diffuse Double Layer Theory.

Very detailed discussions of diffuse double layer theory have been given by Verwey and Overbeek (1948) in their book "Theory of the Stability of Lyophobic Colloids" and again by Overbeek (1952) in "Colloid Science" (edited by Kruyt). In the following resumé only the most salient points will be discussed and only those equations essential to the development of the general theme of the thesis will be given.

Perhaps the most important of the assumptions made by Gouy (1910, 1917) is that ions are point charges of negligible dimensions. For an impenetrable planar surface possessing a charge uniformly smeared over that surface, the Coulombic interaction between the charges in the system is described by Poisson's equation.

$$\frac{d^2\Psi}{dx^2} = -\frac{4\pi\rho}{\varepsilon} \quad \ldots\ldots\ldots\ldots \quad (2)$$

where $\frac{d^2}{dx^2}$ is the Laplace operator for an infinitely large plane interface

Ψ is the electrostatic potential changing from Ψ_0 at the surface to zero in the bulk solution (nominally at infinity).

ρ = charge density

ε = dielectric constant of the dispersion medium.

Gouy (1910) and Chapman (1913) assumed that the average concentration of ions at a given point in the solution is described by Boltzmann's Law

$$n_i = n_{io} \exp\left(-W_i/kT\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where n_i = concentration (ions/ml.) of ions of kind i at a point where the amount of work involved is W_i

n_{io} = bulk solution concentration (ions/ml.)

k = Boltzmann constant

T = temperature in degrees Kelvin

Grahame (1947) proposed that W_i should be regarded as entirely electrical in origin, and used $W_i = z_i e\Psi$ as a definition of potential. The Boltzmann equation then becomes

$$n_i = n_{io} \exp\left(-z_i e\Psi/kT\right) \quad \ldots\ldots\ldots \quad (4)$$

where e = electronic charge

Z = valency, taking the sign of the charge into account, i.e. positive for cations, negative for anions.

However this neglects several work functions involved in the rearrangement of the ionic and molecular structure in a plane at which the potential has been changed. Included among these functions are the work involved in displacing polar solvent molecules from a region of high field strength, the work involved in pushing all other ions in the region a little closer together and the work involved in distorting or displacing the hydration sheath of a solvated ion as a result of the close approach of such an ion to the charged surface. Grahame (1947) considered that the first effect would be extremely small, while Bikerman (1942) showed that the crowding effect was probably not serious enough to invalidate double layer theory. The third effect, will be considered in some detail later in this thesis, because it cannot be neglected when the ion is within one water layer of the charged surface.

Bolt (1955) in an analysis of the validity of Gouy-Chapman double layer theory, considered that some rather misleading conceptions had arisen from the considerations of Bikerman (1942), Grahame (1950), Conway, Bockris and Ammar (1951), Loeb (1951) and Williams (1953), because each of the authors had only considered one of the shortcomings of double layer theory. Since the effects of some of the simplifying assumptions involved in double layer theory offset each other to a certain extent, Bolt considered that all the approximations should be considered simultaneously. Accordingly he divided the work term W_i (equation (3)) into the following components:-

(1) W_1 (most important) = $z_i e \Psi$ i.e. the electrical potential energy of the ion in the electric field.

(2) W_2 - energy resulting from Coulombic interaction between the ions themselves. This term is most important close to a charged surface where the field intensity and thus local ionic concentrations will be considerably higher than at points well removed from the surface.

(3) W_3 - energy of polarization of the ion in the electric field, which will be the sum of distortion polarization and orientation polarization, the latter referring to the partial lining up of already existing dipoles.

(4) W_4 - repulsive energy caused by short-range non-Coulombic interactions between ions.

(5) W_5 - non-Coulombic short-range interaction between an ion and the charged surface.

Bolt's analysis showed that dielectric saturation and ionic polarization effects offset each other almost completely if the surface charge density is less than 2×10^{-7} meq./cm^2. However, for surfaces with higher charge densities, the polarization term increases very rapidly, resulting in ionic concentrations considerably lower than would be expected from Gouy-Chapman theory. Similarly, Coulombic interaction and short range repulsion between ions tend to compensate each other. In this case, Coulombic interaction will be dominant up to concentrations of the order of 1 or 2 molar. It is interesting to note that if a surface charge density of 2 x 10^{-7} meq./cm^2 is confined to a depth of 5 Å immediately adjacent to the surface, the ionic concentration will be approximately 4 molar. Under these conditions short range repulsion will become dominant.

Bolt considered that the energy term W_5 could only be accounted for by introducing the concept of the distance of closest approach between an ion and the charged surface. As a result of this analysis, Bolt was able to conclude that "if the charge density of a colloid does not exceed 2 x 10^{-7} meq./cm^2, the Gouy-Chapman theory will give fairly reliable results, especially if the charge density of the colloid under consideration is constant".

The space charge density, ρ , is given by the algebraic sum of the ionic charges per unit volume:-

$$\rho = \sum z_i e n_i \qquad \ldots\ldots\ldots\ldots \quad (5)$$

Integrating this expression from the surface to infinity gives the total excess charge in the solution per unit area, which is equal and opposite in sign to the surface charge density σ

$$\sigma = -\int_0^\infty \rho \, dx \qquad \ldots\ldots\ldots\ldots \quad (6)$$

By combining equations (2), (4) and (5), the fundamental differential equation for the potential Ψ as a function of the distance from the plane interface is obtained:

$$\frac{d^2\Psi}{dx^2} = -\frac{4\pi}{\varepsilon}\sum z_i e n_{io} \exp(-z_i e\Psi/kT) \qquad (7)$$

Considering a single binary electrolyte, Overbeek (1952) obtained

$$\frac{d\Psi}{dx} = -\sqrt{\frac{8\pi nkT}{\varepsilon}}\left[\exp(ze\Psi/2kT) - \exp(-ze\Psi/2kT)\right] \qquad (8)$$

subject to the boundary conditions that as $x \to \infty, \Psi \to 0$ and thus $\frac{d\Psi}{dx} \to 0$.

Equation (8) was then used to establish a relationship between surface charge density, σ, and surface potential Ψ_0. Integrating equation (6) using Poisson's relation gives

$$\sigma = -\frac{\varepsilon}{4\pi}\left(\frac{d\Psi}{dx}\right)_{x=0} \qquad (9)$$

Inserting the values of $\frac{d\Psi}{dx}$ from equation (9) results in

$$\sigma = \sqrt{\frac{\varepsilon nkT}{2\pi}}\left[\exp(ze\Psi_0/2kT) - \exp(-ze\Psi_0/2kT)\right] \qquad (10)$$

For small values of potential, equation (10) simplifies to

$$\sigma = \sqrt{\frac{\varepsilon nkT}{2\pi}} \cdot \frac{ze\Psi_0}{kT}$$

$$= \frac{\varepsilon}{4\pi}\cdot\sqrt{\frac{8\pi nz^2e^2}{\varepsilon kT}}\cdot \Psi_0 = \frac{\varepsilon K}{4\pi}\cdot \Psi_0 \qquad (11)$$

where $^1/K$ is the Debye characteristic length. For small potentials, the charge and potential are directly related, and the diffuse double layer can therefore be likened to a parallel plate condenser with a separation distance of $^1/K$ between the two plates.

A second integration of equation (8) with the condition $\Psi = \Psi_o$ for $x = 0$ results in

$$Kx = \ln \frac{\left[\exp(ze\Psi/2kT)+1\right]\left[\exp(ze\Psi_o/2kT)-1\right]}{\left[\exp(ze\Psi/2kT)-1\right]\left[\exp(ze\Psi_o/2kT)+1\right]} \qquad (12)$$

Thus if the surface charge density is known, equations (10) and (12) may be used to calculate the electric potential as a function of distance from the surface, for a given bulk electrolyte concentration.

C. Interaction of Diffuse Double Layers.

A case of special practical importance is when two charged particles approach one another, leading to double layer interaction.

A schematic representation of the electric potential between two similar opposed plates, in comparison with that for a single double layer is shown in Fig. 1. The only difference between the two cases lies in the choice of the boundary conditions. In the case of a single double layer the boundary conditions were that the potential and its derivatives were zero an infinite distance away from the surface, while in the case of interacting plates, owing to the symmetry of the

Schematic representation of the electric potential between two similar opposed plates, in comparison with that for a single double layer.

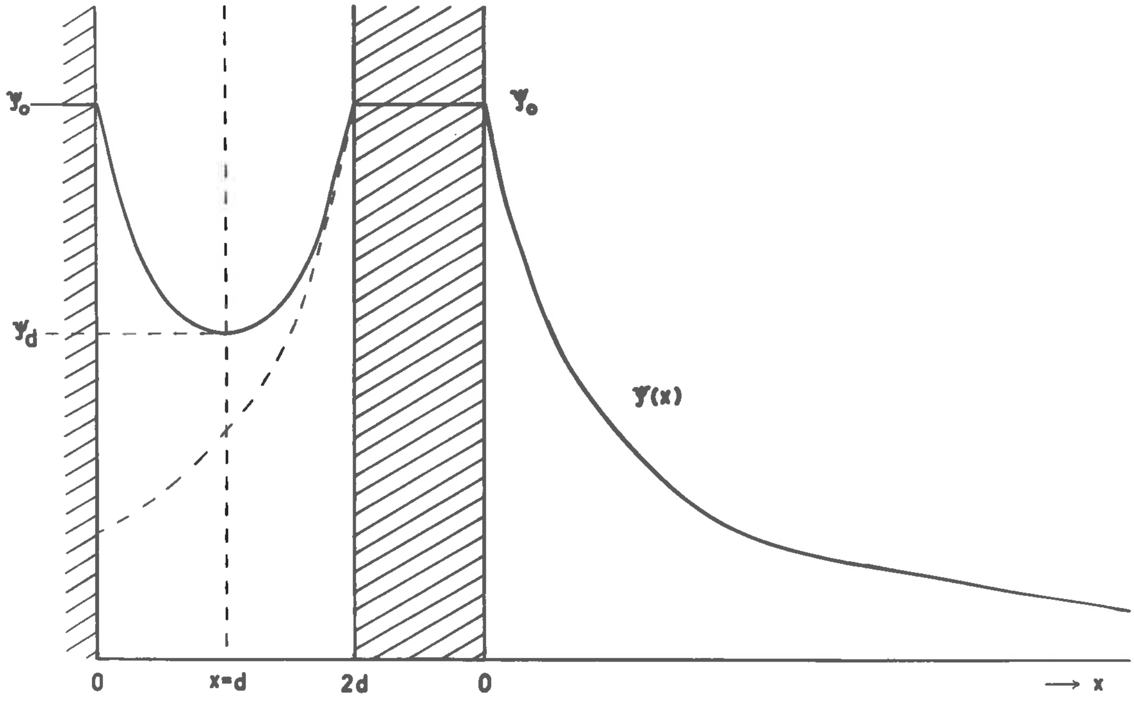

FIGURE 1.

system, the potential has its minimum value halfway between the plates, so that its first derivative will be zero. The equation to be solved is

$$\frac{d^2\psi}{dx^2} = \frac{4\pi}{\varepsilon}\left(n_- z_- \exp\left(\frac{z_- e\psi}{kT}\right) - n_+ z_+ \exp\left(-\frac{z_+ e\psi}{kT}\right)\right) \tag{13}$$

subject to the boundary conditions

$$\psi = \psi_0 \quad \text{for} \quad x = 0$$
$$\psi = \psi_d \quad \text{for} \quad x = d$$
$$\frac{d\psi}{dx} = 0 \quad \text{for} \quad x = d.$$

The distance between the plates is 2d, along the x co-ordinate measured from one of the plates. The first integration of equation (13) leads to

$$\frac{d\psi}{dx} = -\sqrt{\frac{8\pi kT}{\varepsilon}}\sqrt{n_- e^{\frac{z_- e\psi}{kT}} + n_+ e^{\frac{-z_+ e\psi}{kT}} - n_- e^{\frac{z_- e\psi_d}{kT}} - n_+ e^{\frac{-z_+ e\psi_d}{kT}}} \tag{14}$$

Now, for high values of potential, the value of equation (14) is almost completely determined by the positive powers of the exponent, since the negative powers are so small that their influence may be neglected. On restricting the discussion to a symmetrical electrolyte, equation (14) simplifies to

$$\frac{d\psi}{dx} = -\sqrt{\frac{8\pi nkT}{\varepsilon}}\sqrt{2\cosh\frac{ze\psi}{kT} - 2\cosh\frac{ze\psi_d}{kT}} \tag{15}$$

On introducing the variables

$$Y = \frac{ze\psi}{kT}, \quad Z = \frac{ze\psi_0}{kT}, \quad U = \frac{ze\psi_d}{kT}$$

the above equation becomes

$$\frac{dY}{dKx} = -\sqrt{2\cosh Y - 2\cosh U} \tag{16}$$

Integrating this equation between the values Kx = 0, and Kx = Kd leads to a relation between the surface potential Z, the potential between the plates U, and their distance of separation Kd. Verwey and Overbeek (1948) expressed this relation in terms of elliptic integrals

$$Kd = 2e^{-\frac{U}{2}}\left[F\left(e^{-U}, \pi/2\right) - F\left(e^{-U}, \text{arc sine } e^{-\frac{Z-U}{2}}\right)\right] \tag{17}$$

where $F(k,\varphi) = \int_0^{\varphi} \frac{d\alpha}{\sqrt{1-k^2\sin^2\alpha}}$ is a function tabulated by Jahnke and Emde (1945).

The interaction of two opposed double layers and the consequent suppression to a certain extent of each may be considered in terms of a reduction in total charge in the double layer. The mathematical expression for the double layer charge is

$$\sigma = -\frac{\varepsilon}{4\pi}\left(\frac{d\psi}{dx}\right)_{x=0}$$

$$= \sqrt{\frac{\varepsilon n kT}{2\pi}} \cdot \sqrt{2\cosh Z - 2\cosh U} \tag{18}$$

The reduction in double layer charge for large surface potentials is only appreciable when the distance of plate separation is small compared to $^1/K$. As a result of interaction, the free energy of double layer formation becomes less negative (increases), so that work has been gained by the system. Thus, interaction may be considered as the principal cause of repulsion between two parallel plates.

Langmuir (1938), Derjaguin (1940) and Bergmann, Low-Beer and Zocher (1938) obtained approximate expressions for the repulsive force between two plane parallel double layers. They all calculated the force on both sides of one plate, and by subtraction found the resultant force of repulsion. The expression obtained, (Overbeek (1952), for the force acting between two plates per cm^2 is

$$P = 2nkT(\cosh u - 1) \tag{19}$$

This equation contains neither the surface potential (ψ_0 or Z), nor the plate distance 2d, but only the electric potential midway between the two plates (ψ_d or u). However because of the complex relationship between Z , u , and d, (equation 17) it is virtually impossible to integrate equation (19) for a given value of ψ_0 with respect to distance d, in order to evaluate the repulsive potential. Equation (19) may be identified with the van't Hoff osmotic pressure equation with the part in brackets representing the amount by which the concentration of ions at the mid-plane between two interacting plates will exceed the external concentration and therefore the equation gives the osmotic repulsive force or swelling pressure due to this excess of ions.

II. APPLICATIONS OF DIFFUSE DOUBLE LAYER THEORY.

A. Film Thickness.

Diffuse double layer theory was applied by Schofield (1946) to a consideration of the thickness of liquid films on solid surfaces. He derived the following expression for the film thickness adhering to a charged surface:

$$X = \frac{2}{Z\sqrt{\beta C_o}} \text{ arc cot } \frac{2\sqrt{C_o}}{\Gamma\sqrt{\beta}} \tag{20}$$

where Γ = charge density of the surface

$\beta = \frac{8\pi F^2}{\varepsilon RT} = \frac{8.48}{\varepsilon} \times 10^{16}$ cm/meq. at 25°C

C_o = concentration of ions at outer boundary of film.

When $\Gamma \rightarrow \infty$, the extrapolated concentration-distance function of the anions will reach zero, and that of the cations will theoretically reach ∞, in the plane of the surface. Under these conditions arc cot θ = arc cot 0; therefore $\theta = \pi/2$.

Thus, $X_{max} = \frac{2}{Z\sqrt{\beta C_o}} \cdot \frac{\pi}{2}$

$$= \frac{\pi}{Z\sqrt{\beta C_o}} \tag{21}$$

However, in the case of finite charge densities, the extrapolated concentration-distance functions of the anions and cations respectively reach zero and infinity in a theoretical plane, a distance δ behind the charged surface. More expressly, there is a finite anion concentration at the charged surface. Expansion of equation (20) leads to

$$X = \frac{\pi}{Z\sqrt{\beta C_0}} - \frac{4}{Z\beta\Gamma} + \frac{16C_0}{Z\beta^2\Gamma^3} - \frac{64C_0^2}{Z\beta^3\Gamma^5} \qquad (22)$$

As a result of the finite charge density the film thickness measured from the charged surface is reduced by a factor $X_{max}-X = \delta$, viz.

$$\delta = \frac{4}{Z\beta\Gamma} - \frac{16C_0}{Z\beta^2\Gamma^3} + \frac{64C_0^2}{Z\beta^3\Gamma^5} - \cdot \cdot \cdot \cdot \qquad (23)$$

Neglecting second and following order terms, since the charge density is large but not infinite, $\delta = \frac{4}{Z\beta\Gamma}$ may be identified with the correction term appearing in Schofield's negative adsorption equation (see later in this thesis).

Writing p_0 for the van't Hoff pressure at the outer surface of the film leads to the relation (as long as C_0 is small)

$$p_0 = RTC_0 \qquad (24)$$

p_0 is then the excess of hydrostatic pressure at the outer surface of the film over that of the bulk liquid in equilibrium with it at the same horizontal level. p_o will also refer to the swelling pressure between two opposed surfaces separated by a distance 2X. Film thicknesses calculated by Quirk (1962) for a 1:1 electrolyte at different concentrations and hydrostatic pressures are shown in Table 1.

In discussing the necessity for the film thickness approach, Schofield (1946) stated:

"In these systems it is important to distinguish broadly between irreversible shrinkage due to re-arrangement of the particles, and reversible shrinkage associated with the dependence of film thickness on pressure." It is very evident that much of the work seeking to verify Schofield's film thickness theory has failed to take this possibility into consideration. Aylmore and Quirk (1959) re-iterated these ideas for clay-water systems and furthermore considered that the central problem in the interpretation of much swelling data is to distinguish between water directly associated with clay surfaces and water which is simply enmeshed in a gel structure.

A special feature of Schofield's film thickness theory is that it has a similar basis to the negative adsorption theory (see p.19) and hence consideration of the film thickness approach will lead to a better understanding of the negative adsorption equation.

TABLE 1

FILM THICKNESS (Å) FOR A 1:1 ELECTROLYTE AT DIFFERENT CONCENTRATIONS AND HYDROSTATIC SUCTIONS. (Quirk, 1962)

Pressure	Electrolyte concn. (meq./ml.)			
cm H_2O	0.1	0.01	0.001	0.0001
1	60	150	360	770
10	48	115	240	440
100	36	77	125	145
1,000	24	39	44	48
10,000	12	12	14	15

* For a 2:1 electrolyte film thicknesses of about one-half the values in Table 1 would be expected.

B. Repulsion of Anions.

1. Simple Donnan Theory.

The characteristic feature of the Donnan membrane equilibrium is the unequal distribution of cations and anions which results from the presence of an ion or charged molecule restrained from diffusing to all parts of the electrolyte system. Considering the fixed negative charge on a large anion as z, the internal anion concentration as y and the external anion concentration as x (all in millimoles per ml.) the following equation is obtained for a 1:1 electrolyte

$$y\ (z + y) = x^2 \qquad \ldots\ldots\ldots\ldots\ldots \qquad (25)$$

The corresponding equation for a 2:1 electrolyte is

$$y^2\ (z + y) = x^3 \qquad \ldots\ldots\ldots\ldots\ldots \qquad (26)$$

On identifying z with the exchange capacity E per unit volume of a negatively charged colloid, the maximum possible exclusion becomes E/2 for monovalent cation systems, and E/3 for divalent cation systems.

2. Schofield's Negative Adsorption Theory.

(a) Derivation.

The Gouy-Chapman diffuse double layer theory was used by Schofield (1947) and Overbeek (1956) to derive expressions for the negative adsorption or repulsion of anions from single negatively charged surfaces. Schofield's equation was derived for a single charged interface, but he was able to extend its applicability by introducing a number of qualifying conditions. Overbeek's treatment was more general and included the case of anion exclusion from interacting double layers.

Schofield's (1947) equation describes the repulsion (negative adsorption) of anions from a negatively charged surface in terms of a "depth of liquid" immediately adjacent to the surface from which the anion may be considered totally excluded. However, the actual concentration-distance function of the anions is as shown in Fig. 2 (Verwey and Overbeek, 1948). Both anion and cation distribution functions are shown for a surface potential of -76.8 mV, together with a plot of the parameter $ze\Psi/kT$ against the dimensionless function Kx. It may be noted that the anions become more sparse as the surface is approached, resulting in the anion deficit which Schofield (1947) referred to as negative adsorption. The surface ABC in Fig. 2 characterizes the distribution of the counter-charge, which is due to a local excess of cations ABD and a deficit of anions CBD with respect to the composition of the liquid phase far away from the surface. Thus

$$\Gamma = \Gamma_{+} + \Gamma_{-} \qquad (27)$$

where Γ is the surface density of charge, Γ_{+} is the positive adsorption of cations per unit surface and Γ_{-} is the negative adsorption of anions per unit surface.

Electric potential function ($ze\Psi/kT$) together with cation and anion concentrations in relation to the distance x from a negatively charged surface. ($Z = ze\Psi_0/kT = 3$; $\Psi_0 = 76{\cdot}8\,mV$.)

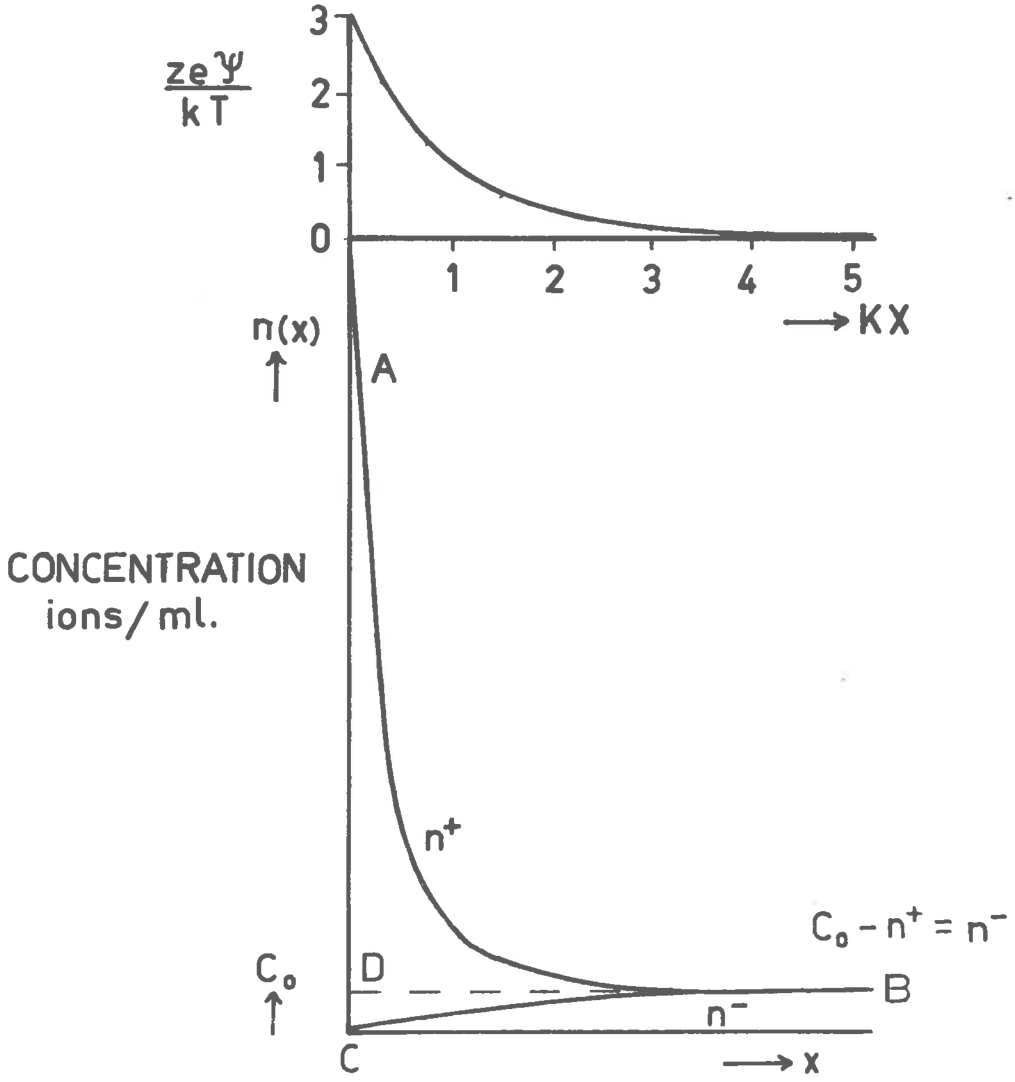

FIGURE 2.

The derivation of Schofield's equation remained unpublished until 1962 (Shone). Equation (8) relating the variation of electric potential ψ with distance from the surface x for a symmetrical electrolyte may be re-written as

$$\frac{d\psi}{dx} = \sqrt{\frac{32\pi n_o kT}{\varepsilon}} \sinh\left(-\frac{ze\psi}{kT}\right) \tag{28}$$

Putting

$$\beta = \frac{8\pi F^2}{1{,}000\varepsilon RT}, \quad q = -\frac{ze\psi}{2kT} \text{ and } C_o = \frac{1{,}000 z n_o}{N}$$

where F is the Faraday (= 2.892×10^{11} e.s.u./meq.), C_o the bulk concentration in meq./ml. and N is Avogadro's Number (= 6.023×10^{23}), equation (28) may be written as

$$\frac{dx}{dq} = \frac{1}{\sqrt{z\beta C_o}} \operatorname{cosech}\left(-\frac{ze\psi}{2kT}\right) \tag{29}$$

$\frac{1}{\sqrt{z\beta C_o}}$ is identical with the Debye-Hückel parameter $^1/K$. If the distance x is measured from an imaginary surface where $\psi = -\infty$, it follows that

$$x = -\frac{1}{\sqrt{z\beta C_o}} \ln \tanh\left(-\frac{ze\psi}{4kT}\right) + C \tag{30}$$

When $x = o$, $q = \infty$, and therefore the integration constant C is zero. The local concentration of anions at any point in the double layer, C^- is given by the Boltzmann equation

$$C^- = C_o \exp\left(-\frac{ze\psi}{kT}\right) \tag{31}$$

Combining equations (30) and (31) and rearranging gives

$$C^{-} = C_o \tanh^2\left(\frac{x}{2}\right)\sqrt{z\beta C_o} \qquad (32)$$

Introducing δ (see equation (23)), the number of anions per cm^2 surface, S^{-} is given by integrating equation (32) between the limits δ and $X+\delta$

$$S^{-} = C_o \int_{\delta}^{X+\delta} \tanh^2 \frac{\sqrt{z\beta C_o}}{2} . x \, dx$$

$$= C_o \left[x - \frac{2}{\sqrt{z\beta C_o}} \tanh \frac{\sqrt{z\beta C_o}}{2} . x \right]_{\delta}^{X+\delta} \qquad (33)$$

Here X is the thickness of the film associated with a single plane surface, or half the distance between two plane parallel surfaces. Equation (33) will only be valid if the concentration of anions at a distance X from the surface is nearly equal to C_o, i.e. where there is virtually no double layer interaction. The surface deficit of anions, Γ_{-} is given by

$$\Gamma_{-} = XC_o - S^{-} \qquad (34)$$

Combining equations (33) and (34) and inserting the limits gives

$$\frac{\Gamma_{-}}{C_o} = \frac{2}{\sqrt{z\beta C_o}} \tanh \frac{\sqrt{z\beta C_o}}{2}(X+\delta) - \frac{2}{\sqrt{z\beta C_o}} \tanh \frac{\sqrt{z\beta C_o}}{2} . \delta \qquad (35)$$

Schofield used the approximation $\delta = \frac{4}{z\beta\Gamma}$ (equation (23)) together with a series of qualifying conditions, to be discussed below, to obtain the following final relation:

$$\frac{\Gamma_-}{C_o} = \frac{2}{\sqrt{z\beta C_o}} - \frac{4}{z\beta\Gamma} \qquad (36)$$

Shone (1962) published similar derivations for the case of asymmetrical 1:2 and 2:1 electrolytes. The final equations were as follows

1:2 electrolyte $$\frac{\Gamma_-}{C_o} = \frac{6^{1/2}}{\sqrt{z\beta C_o}} - \frac{4}{z\beta\Gamma} \qquad (37)$$

2:1 electrolyte $$\frac{\Gamma_-}{C_o} = \frac{12^{1/2} - 2}{\sqrt{z\beta C_o}} - \frac{4}{z\beta\Gamma} \qquad (38)$$

Schofield (1947) generalized the negative adsorption equation into the form*

$$\frac{\Gamma_-}{C_o} = \frac{q}{\sqrt{z\beta C_o}} - \frac{4}{z\beta\Gamma} \qquad (39)$$

where q is a constant for a particular electrolyte type, depending on the ratio of the valencies of the attracted and the repelled ions. The quantity $\frac{\Gamma_-}{C_o}$ has the dimensions of cm. (meq./cm^2/meq./cm^3) and is thus a measure of the depth of liquid per unit surface area adjacent to the negatively charged surface from which the anion of the electro-

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* The equation given by Bolt and Warkentin (1958) is identical with that of Schofield (equation (39), this thesis). Unfortunately, their equation appears different, because they have used molar instead of normal concentrations.

lyte may be considered totally excluded. This is equivalent to considering that the bulk concentration is reached at a depth from the surface, rather than at an infinite distance from the surface where the electric potential approaches zero.

Anion repulsion may be expressed as a volume of water from which chloride is totally exchded. This volume which is readily determined experimentally is equal to the product of the charged surface area of the colloid A_o and $\frac{\Gamma_-}{C_o}$. The measured volumes plotted against $\frac{q}{\sqrt{z\beta C_o}}$ should, according to equation (39), give a straight line the slope of which is the surface area of the charged material repelling the chloride ions.

Schofield (1947) considered that equation (39) was particularly suitable for comparison with experiment because the variable term $\frac{q}{\sqrt{z\beta C_o}}$ depends only on the concentration, but not on the magnitude of the surface charge, provided that Γ is large enough for the constant term $\frac{4}{z\beta\Gamma}$ to be small in comparison with $\frac{q}{\sqrt{z\beta C_o}}$.

(b) Conditions of Applicability.

The conditions under which equation (39) can be used are best considered under two categories.

(1) When the double layers associated with two opposed plates interact, the particle separation may be such that full development is impeded, and hence, Schofield has set down values of $z\beta\Gamma X$ to define the conditions of applicability. Two extreme cases are readily recognized.

The first case occurs when the plates are so far apart that the full development of the diffuse double layers is virtually attained. Thus if the charge density Γ is 1×10^{-7} meq./cm^2 double layer development occurs if $X > 30/z\beta\Gamma$ (i.e. $X > 30$ Å). The opposed plates will thus need to be separated by at least 60 Å (Fig. 3 (a)). Further, for unimpeded double layer development to occur, $\frac{q}{\sqrt{z\beta C_o}}$ must lie between $15/z\beta\Gamma$ and $X/2$. Thus for $\Gamma = 1 \times 10^{-7}$ meq./cm^2, the lower limit of applicability is that $\frac{q}{\sqrt{z\beta C_o}}$ must be > 15 Å, i.e. the electrolyte concentration C_o must be < 0.17 meq./ml. For a charge density of 1×10^{-8} meq./cm^2, the plates must be separated by $2X > 600$ Å, and the lower limit of applicability given by $\frac{q}{\sqrt{z\beta C_o}} > 150$ Å will only hold for electrolyte concentrations < 0.0017 meq./ml. Identifying $\frac{q}{\sqrt{z\beta C_o}}$ with $X/2$, means that the plate separation for complete double layer development (no interaction) to occur between opposed plates must be equal to $2X = 4 \times 2/\sqrt{z\beta C_o} = 8/\sqrt{z\beta C_o} = 8/K$, which is the condition stated by Schofield (1949).

The second case occurs when the plate separation is such that the distance of separation of the surfaces is about the same as the separation of charges on the surfaces. In this situation there is a uniform volume distribution of charge, and hence the simple Donnan equation can be applied. Schofield and Talibuddin (1948) derived the following equation, subject to the condition $z\beta\Gamma X < 10$, to describe anion exclusion in terms of a simple Donnan relation:-

$$\frac{\Gamma}{C_oX} = \left(1 - \frac{\Gamma_-}{C_oX}\right)^{-p} - \left(1 - \frac{\Gamma_-}{C_oX}\right) \qquad (40)$$

Conditions of applicability of Schofield's negative adsorption equation.

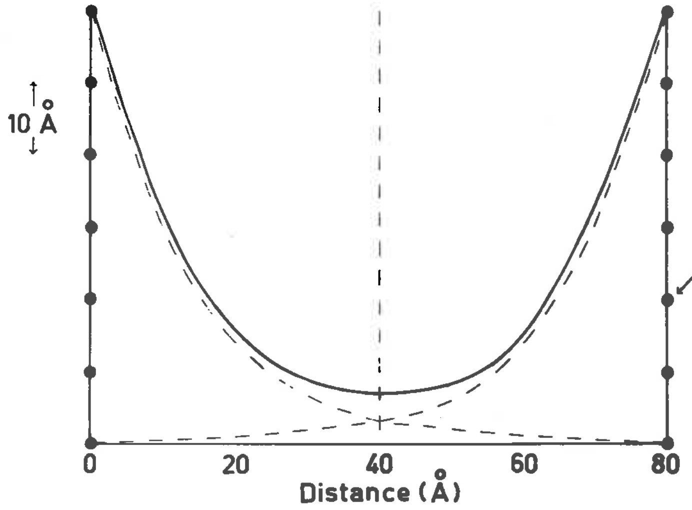

Distance of separation of surfaces large compared to distance of separation of charges on those surfaces.

FIGURE 3(a)

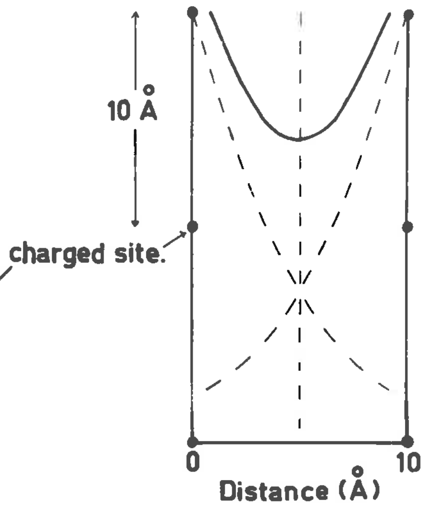

Separation of charges equal to separation of surfaces.

FIGURE 3(b)

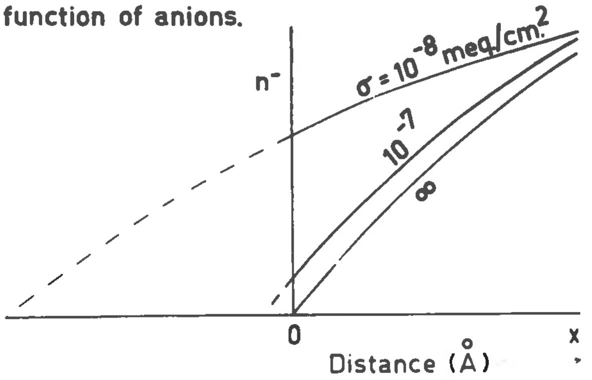

Extrapolated concentration – distance function of anions.

FIGURE 3(c)

where p is the ratio of cationic to anionic valency. If the charge density Γ is 1×10^{-7} meq./cm^2, the distance of charge separation on the surfaces will be about 13 Å, while the distance of plate separation (2X) will be less than 20 Å (i.e. if $z\beta\Gamma X < 10$, $2X < 20$). This system thus approaches a uniform volume distribution of charge (Fig. 3 (b)). If $z\beta\Gamma X$ is too small, equation (39) will not be valid for any value of C_o.

(2) The correction term $\frac{4}{z\beta\Gamma}$ has been introduced to allow for the fact that the theory predicts that the concentration of anions will not effectively reach zero until some distance behind the charged surface (Fig. 3 (c)). The magnitude of this correction term has been considered in relation to the magnitude of the diffuse double layer development. Schofield (1947, 1949) showed that when the correction term $\frac{4}{z\beta\Gamma}$ is more than one-quarter of the main term $\frac{q}{\sqrt{z\beta C_o}}$ application of equation (39) becomes inadequate. Thus for a charge density of 1×10^{-7} meq./cm^2, $\frac{4}{z\beta\Gamma} \simeq 4$ Å while for $\Gamma = 1 \times 10^{-8}$ meq./cm^2, $\frac{4}{z\beta\Gamma} \simeq 40$ Å. For an electrolyte concentration of 0.01 meq./ml., where $\frac{q}{\sqrt{z\beta C_o}} \simeq 61$ Å, Schofield's equation will hold in the first case, but will be unsatisfactory in the second case.

It is of interest to note that the above conditions generally seem to be met in practice, irrespective of the average charge density, i.e. wherever anion exclusion occurs, the charge density is high enough for the conditions to be satisfied.

3. Overbeek's Generalized Donnan Expression.

Overbeek (1956) quantitatively treated the unequal distribution of ions in the vicinity of a charged surface and derived an equation in which the deficit of repelled ions in the double layer is related to the surface potential. He expressed the ion distribution in terms of the fraction of the surface charge of the colloid which is compensated by an excess of counter-ions and a deficit of co-ions respectively. From Fig. 2, it may be seen that the concentration-distance functions of both cations and anions follow the exponential Boltzmann distribution. At any plane, parallel to the surface, the electric potential is constant, and the ion concentration product of cations and anions is constant. Thus,

$$C^{+} . C^{-} = C_{o}^{2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \ (41)$$

where C^{+} is the local concentration of cations, and C^{-} that of anions in the given plane. This is a generalized expression of the Donnan equation (25).

The excess of cations and deficit of anions adjacent to a negatively charged surface were found by integrating the local concentrations over the double layer volume, and subtracting the bulk concentration taken over the same volume. Accordingly, Overbeek (1956) derived the following expression for the fraction of the particle charge compensated by a deficit of co-ions :

$$\alpha_- = \frac{1 - \exp(ze\Psi_0/2kT)}{\exp(-ze\Psi_0/2kT) - \exp(ze\Psi_0/2kT)} \qquad (42)^*$$

For very small values of surface potential, α_- is equal to 0.50, consistent with mirror image distributions of accumulated cations and repelled anions. However, as the surface potential is increased, an increasingly larger proportion of the particle charge is balanced by the excess of cations (see Fig. 2).

The case of interacting double layers was also treated by Overbeek (1956). Since the value of the mid-plane potential is greater than that at the same distance from a single charged plate, the fraction of the particle charge compensated by a deficit of co-ions is smaller than for a single charged plate. The relationship obtained by Overbeek for interacting double layers was:

$$\alpha'_- = \frac{\left[E(e^u, \pi/2) - E(e^u, \arcsin e^{\frac{z-u}{2}})\right] - (1 - e^u)\left[\cdots\cdots\right]}{e^{u/2}\sqrt{e^z + e^{-z} - e^u - e^{-u}}}$$

$$\left[F(e^u, \pi/2) - F(e^u, \arcsin e^{\frac{z-u}{2}})\right] \qquad (43)$$

---

* (1) See Appendix I for derivation of equation (42).

(2) Overbeek's (1956) final expression was incorrect, due to some confusion in sign. Edwards and Quirk (1962) used the correct expression to calculate the fraction of the particle charge compensated by a deficit of co-ions, although they recorded Overbeek's equation in error. Helmy (1963) also recorded this expression incorrectly.

where $u = ze\Psi_d/kT$ with Ψ_d equal to the mid plane potential

$z = ze\Psi_o/kT$

$F(k,\varphi)$ = elliptic integral of the first kind, (Jahnke and Emde, 1945).

$E(k,\varphi)$ = elliptic integral of the second kind (Jahnke and Emde, 1945).

Comparison of α'_- for interacting plates, with α_- for a single negatively charged plate gives the anion deficit as a fraction of that obtained when double layer development is unrestricted.

Overbeek (1956) also considered the case of very strong interaction of double layers and concluded that, under these conditions, a classical Donnan situation is reached, with the local concentrations of ions virtually invariable. The potential drop between the surface and the mid-plane will be very small.

4. Anion Exclusion by Charged Surfaces.

The equilibrium measurements of Proctor (1914) on the system dilute hydrochloric acid and gelatin conform to a simple Donnan system. Schofield (1946) regarded this as evidence that the positively charged groups of the protein have a substantially uniform volume distribution in the gel. He also pointed out that the Congo Red system investigated by Donnan and Harris (1911) did not even approximately obey the theory because the negatively charged groups were clustered together in micelles.

The first application of the Donnan concept to negative adsorption by soil systems was made by Mattson (1929) is an effort to explain results obtained with a series of bentonites and soil colloids. Schofield (1946, 1949) applied his negative adsorption theory to Mattson's data, and obtained a surface area for montmorillonite of 470 m^2/g. (cf. about 800 m^2/g. for a complete dispersion into independent plates). He considered this agreement was remarkably good, particularly when it is realized that for the full deficit to be developed two opposed surfaces have to be separated by a distance of $^8/K$. Bolt and Warkentin (1956, 1958) measured negative adsorption from Wyoming bentonite suspensions, and obtained areas less than the expected 700-800 m^2/g. They attributed the deviation to the presence of positive charges. Edwards and Quirk (1962) obtained surface areas of 560 m^2/g. for sodium and about 100 m^2/g. for calcium Wyoming bentonite. These results (to be discussed later in this thesis) were attributed to the association of clay plates in crystals, as had been suggested by X-ray spacing measurements of Norrish and Quirk (1954) and Norrish (1954).

The application of Donnan theory to soil systems was critically reviewed by Davis (1942) who concluded by saying he "doubted that soil properties can be adequately explained in terms of Donnan equilibria in preference to other hypotheses. It is suggested that the importance of the Donnan equilibrium as a regulative principle in soil chemistry has been greatly overemphasized." Babcock (1960), in agreement with Davis (1942), considered there were no adequate reasons for accepting or rejecting the Donnan theory in such systems. Recently, Posner and Quirk (1964) measured the adsorption of water and concomitant exclusion of electrolyte from concentrated solutions by montmorillonite and illite and obtained considerable deviations from the expected simple Donnan behaviour. The amount of exclusion was always greater than predicted by Donnan theory, because of differences in the water structure in the immediate proximity to the surface and in the bulk solution.

Many attempts, with varying amounts of success, have been made to describe negative adsorption in cation exchange resin systems. Baumann and Eichhorn (1947) showed negative adsorption could be accounted for satisfactorily by Donnan equilibrium considerations. However, Gregor, Gutoff and Bregman (1951) and Gleuckauf and Watts (1962) were unable to describe ion exclusion from resins by means of a Donnan equilibrium. The latter authors concluded that: "the fractional power law of the counter-ion concentration is a phenomenon which is inherent in the nature of the organic ion exchangers which have been tested. However, the Donnan law must apply to any two homogeneous phases; one is therefore forced to the conclusion that ion exchanger polymers (certain cross-linked ones, possibly also linear ones) cannot be considered as homogeneous phases. Consequently none of the equilibrium relationships between cross-linked ion exchangers and solutions need be governed by the usual activity product relationships.

This conclusion may have important consequences because it may mean that the successes obtained with previous theories for ion exchangers (Gregor, 1951; Glueckauf, 1952; Boyd and Soldano, 1953, etc.), including those dealing with the exchange equilibria of two ions, all of which are based on the Donnan law, may have been to some extent fortuitous, and may require modification." However, Barrer and Meier (1958) showed that the exclusion of ions by Zeolites was governed by a simple Donnan equilibrium.

Overbeek (1952, 1956) successfully applied his generalized Donnan expression for anion exclusion to the repulsion of bromide ions from negatively charged gum arabic sols, measured by Klaarenbeek (1946). Even at high concentrations of gum arabic, bromide exclusion followed Overbeek's relationship for interacting double layers. The data fitted this model far more effectively than the simple Donnan model. Schofield and Talibuddin (1948) measured chloride exclusion from several samples of jute fibre, and found that where the distance of separation of surfaces was large compared to the separation of charges, the results conformed to equation (39). Overbeek's anion exclusion theory would also satisfactorily interpret these results. However, where a uniform volume distribution of charge was approached, simple Donnan theory (equation (40)) satisfactorily described the data.

The results of Shone's (1962) experiments on the equilibrium distribution of ions between a phenol-formaldehyde sulphonate ion-exchange resin and external electrolyte solutions were more satisfactorily described by Schofield's equation (39) than by the Donnan theory.

The average separation of surfaces (approximately 60 Å) was considerably greater than the charge separation of about 9 Å, resulting in a wide variation in electrical potential and local concentration within the resin, under which conditions Donnan's theory does not apply. However, Schofield's equation also failed at low external electrolyte concentrations, presumably because of the overlapping of double layers.

III. ION ADSORPTION AT CHARGED SURFACES.

A. Stern Theory.

The simple Gouy-Chapman diffuse double layer theory discussed above is limited in its applicability to real colloid systems because of the assumptions involved. The assumption that ions are point charges means that they can approach a charged surface without any limit. The influence of ionic dimensions on double layer theory will be greatest near the charged surface with the result that corrections for ion size become most important in the ionic layers immediately adjacent to the surface. In many cases, it will be sufficient to only consider the dimensions of the first layer of ions, because the concentrations and potentials will then have dropped to values low enough to warrant the approximation that ions are point charges. If such a limit was not imposed, a double layer potential of 300 millivolts and a 1-1 electrolyte concentration of 10^{-3} meq./ml. would, by the application of equation (4), lead to a local concentration of counter ions near the surface of

$C = 10^{-3}.e^{12} = 160$ meq./ml., which is an impossibly high concentration.

Stern (1924) divided the spatial charge in the dispersion medium near a charged surface into two parts. The first known as the Stern layer consists of a layer of ions adsorbed at the surface, which may be considered to be located in a plane at a small distance $d (\leqslant 5 \mathring{A})$ from the surface. The second part is the Gouy-Chapman diffuse layer which is displaced a distance d away from the charged surface. A schematic representation of the manner in which the potential varies with distance from the charged surface, according to the Stern theory is shown in Fig. 4. The total potential drop Ψ_o is seen to be divided into an exponential potential drop of Ψ_d over the diffuse part of the double layer, and a linear drop of $(\Psi_o - \Psi_d)$ over the Stern layer.

Stern (1924) also considered in quite general terms the possibility of specific adsorption of ions at the charged surface, and considered that these ions were also located in a plane a distance d away from the surface. In a manner analogous to the derivation of Langmuir's (1916, 1917, 1918) adsorption isotherm, Stern developed an equation describing the surface charge associated with the adsorbed ionic layer:-

$$\sigma_1 = \frac{N_s z e}{1 + \frac{N}{Mn} e^{-\frac{ze\Psi_d + \varphi}{kT}}} \qquad (44)$$

Schematic representation of the double layer according to the theory of Stern.

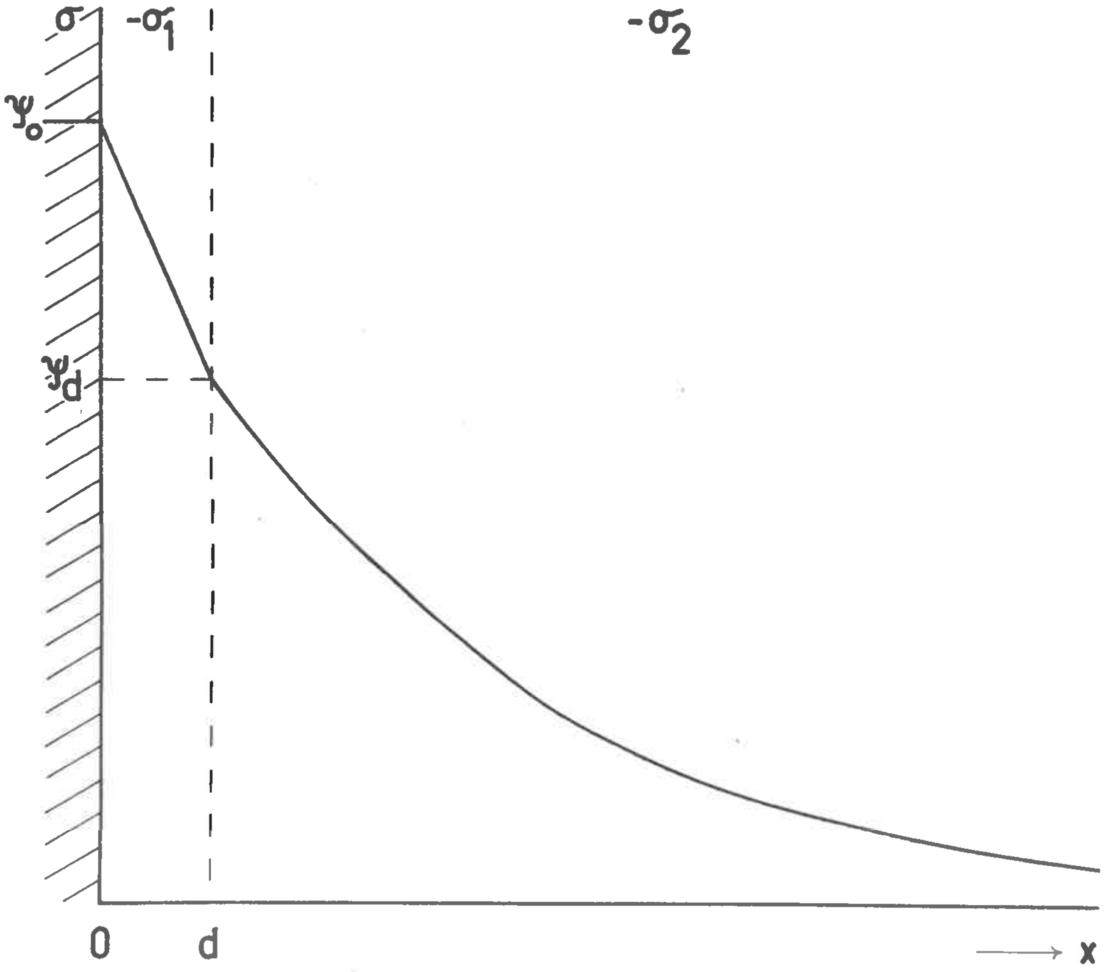


FIGURE 4.

where N_S = number of adsorption spots per cm^2 surface

N = Avogadro's Number

M = molecular weight of solvent

φ = specific adsorption potential of the counter ion adsorbed to the wall

n = bulk electrolyte concentrations (ions/ml.)

The charge in the diffuse part of the double layer was derived earlier (equation (10)):-

$$\sigma_2 = \sqrt{\frac{\varepsilon n k T}{2\pi}}\left[\exp\left(\frac{ze\psi_d}{2kT}\right) - \exp\left(-\frac{ze\psi_d}{2kT}\right)\right] \tag{45}$$

The total charge in the complete double layer is equal to the sum of the charges in the Stern layer and the Gouy-Chapman diffuse layer

$$\sigma = \sigma_1 + \sigma_2 \tag{46}$$

Verwey and Overbeek (1947) showed, by means of a theoretical analysis that for dilute electrolyte solutions and small values of the adsorption potential φ, that only a small part of the total potential drop occurs in the Stern layer. However, in concentrated solutions there is a large potential drop in the Stern layer. In an endeavour to demonstrate how realistic values of adsorption potential are, Parsons (1954) discussed an equation proposed by Stern (1924) relating the standard electrochemical free energy of adsorption to the potential difference between the adsorbed monolayer and the bulk solution, as well as to specific adsorption forces. Stern expressed the relation in the form

$$\overline{\Delta G^{o}_{ads}} = \Delta G^{o}_{ads} + ze\Psi_1 \tag{47}$$

where Ψ_1 was considered to be the electric potential in the monolayer, and ΔG^{o}_{ads} is termed the specific adsorption potential. Parsons concluded that it would be difficult to frame a suitable definition of Ψ_1 to give a logical meaning to the specific adsorption potential.

The problem of the interaction of diffuse double layers will not be seriously affected by the neglect of the Stern layer, because in the majority of cases, interaction is essentially restricted to the inter-penetration of two opposed diffuse layers.

B. Grahame's Compact Double Layer.

Grahame (1947) modified the Stern layer adjacent to a charged surface by distinguishing between the plane of centres of a layer of specifically adsorbed ions and the limit of the diffuse layer. He considered that ions bound to a mercury surface either by covalent bonds, or by van der Waal's forces are not separated from the surface by a layer of solvent molecules. On the other hand, ions not bound at the surface were assumed to be separated from the surface by a solvent sheath, at least when the solvent is water. Implicit in this definition is the feature that when an ion is bound, energy is required to displace the solvent on the interface side of the ion. Grahame designated the locus of centres of the adsorbed ions as the inner Helmholtz plane (I.H.P.) and the locus of centres of hydrated ions in contact with the surface as the outer Helmholtz plane (O.H.P.) - see Fig. 5. Grahame's concept that the O.H.P. is the same for all ions is difficult to reconcile with his proposed model because it does not take the variable size of ions into account (e.g. compare size of solvated Li and Cs ions).

Adamson (1960) considered the implications of potential determining ions on the adsorbed layer on silver iodide and gold sols. He postulated that these potential determining ions were desolvated and completely removed from solution, or were chemically associated with the surface. He regarded the Stern layer as a second rather immobile layer of solvated ions held fairly strongly by electrostatic and non-specific chemical forces. This model is thus essentially the same as that of Grahame (1947). In further considerations of this region, Grahame's terminology will be adopted.

C. Ion Binding.

1. Ion-Pair Formation.

Bjerrum (1926) considered that the failure of the Debye-Hückel (1923, 1924) theory in concentrated solutions of strong electrolytes was due to the assumption that in regions where the electrostatic potential is very large, no ions are close to other ions. He postulated the presence of ion-pairs as a result of purely electrostatic attraction between ions of opposite charge. The Bjerrum ion pairs are not true undissociated molecules in the sense defined

Grahame's compact double layer.

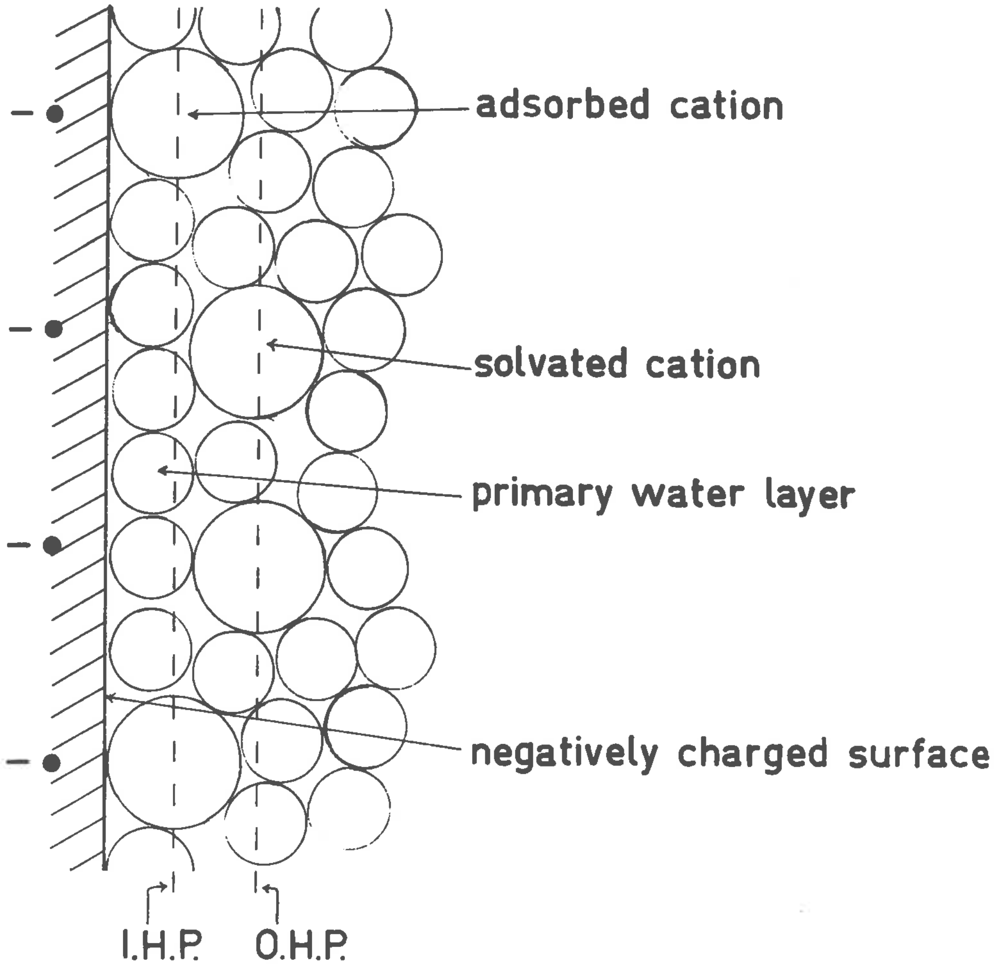


FIGURE 5.

by Arrhenius (1887), but are nevertheless assumed to behave in a manner similar to undissociated molecules and to have no electrostatic effect on any free ions present in the system. Reiss (1956) and Fuoss (1958) considered that Bjerrum's definition of an ion pair is purely arbitrary, because ions which are not in actual physical contact are considered as associated pairs.

The concept of actual physical contact was used by Sadek and Fuoss (1954) in defining an ion pair. These authors divided the ion pairing process into two parts, the first of which is considered to be ion pairing in the Bjerrum sense

$$A^{+} + B^{-} (+S) \rightleftharpoons A^{+}SB^{-}$$

The second step is the process of desolvation

$$A^{+}SB^{-} \rightleftharpoons A^{+}B^{-} + S$$

where S denotes solvent molecules. Denison and Ramsey (1955), Gilkerson (1956) and Fuoss (1959) all proposed equivalent ion pair theories in which the actual ions are in physical contact.

The distribution of ions in the adsorbed layer immediately adjacent to a charged surface has been considered in terms of ions present immediately at the surface, and ions that are one water molecule removed from the surface (Grahame, 1947). It is considered that ions bound at the immediate surface form "Fuoss-type" ion pairs in the I.H.P. while those bound in the O.H.P. one water layer removed from the charged surface form "Bjerrum-type" ion pairs. Furthermore, both types of ion pairs may exist in equilibrium. By definition neither the Fuoss nor the Bjerrum ion pairs can be involved in diffuse layer formation because the forces holding the ion are so large compared with kT, that the counterions do not have the mobility to enable them to move from the surface and permit diffuse double layer formation by the charged surface.

A second equilibrium will also exist between free ions with fully developed ionic atmospheres which exist in the diffuse part of the double layer and the Bjerrum associated surface ions. These free ions are indistinguishable from the bulk electrolyte ions, possessing the same mobility which allows them to move from one diffuse double layer into another.

2. Ion-Binding by Polyelectrolytes.

Two different models have been advanced to account for ion-binding phenomena in polyelectrolytes. The first model (Fuoss, 1954; Oosawa, Imai and Kagawa, 1954; Kagawa and Katsuura, 1955; Wall, 1957) is based on the occlusion of counterions by the coiled polyion, whereas the second model (Harris and Rice, 1954; Strauss, Gershfeld and Spiera, 1954; Strauss, Woodside and Wineman, 1957; Strauss and Wineman, 1958; Strauss and Ander, 1958; Strauss and Bluestone, 1959; Strauss and Ross, 1959 a, b; Inagaki and Oda, 1956 and Inagaki, Hotta and Hirami, 1957) is based on the binding of counterions by localization in the vicinity of the fixed charges of the polyion. The second model only will be briefly considered, since the first is clearly not applicable to binding on the planar charged surfaces of clay minerals.

The site-binding model is an extension of the ion-pair model for simple electrolyte solutions discussed above. Counterions are localized on or near charged sites by the high electrostatic potential originating in the fixed charges. Harris and Rice's (1954) treatment considered the electrostatic free energy of polymers containing discrete charges rather than continuous charge distributions. A definite free energy change is associated with the formation of each ion pair, and polymer charges thus paired may be regarded as effectively uncharged groups. A consequence of this type of binding is that the nett charge involved in diffuse layer formation will be less than the charge of the polymer.

The experiments of Huizenga, Grieger and Wall (1950) show conclusively that the counterions of polyacrylic acid are intimately associated with it, due to the formation of ion pairs in regions of high electrostatic potential. There is considerable evidence supporting the ion pair concept from sedimentation measurements on polymethacrylic acid (Howard and Jordon, 1954; Kraut, 1954), electrophoretic measurements on polyvinylpyridinium bromide (Strauss, Gershfeld and Spiera, 1954) and electrophoretic measurements on polyacrylic acid (Wall, Terayama and Techakumpuch, 1956). Donnan membrane equilibria have also been used to measure the extent of ion binding to polyphosphates (Strauss et al., 1954, 1957; 1958 a, b, 1959 a, b).

3. Ion-Association on Clay Mineral Surfaces.

The determinations of zeta potential made by Mattson (1926) indicated a degree of dissociation of sodium bentonites of 0.17 per cent. In an endeavour to interpret his results on Donnan systems prepared from bentonite gels and solutions of sodium salts, Mattson (1929) assumed that the exchangeable sodium ions were incompletely dissociated from the bentonite surfaces. Davis (1942) made similar calculations to those of Mattson; the apparent degrees of dissociation are given in Table 3. The degree of dissociation is seen to increase with electrolyte concentration. Mattson (1929) suggested that in pure bentonite suspensions the colloid is only very slightly dissociated. He also suggested that in more concentrated electrolytes, the potential of the colloidal particle is decreased, so that the counterions are able to dissociate more readily from the surface. This unexpected behaviour was also referred to by Overbeek (1956) in interpreting Donnan potentials determined by Klaarenbeek (1946) in systems containing sodium arabinate and KBr. Overbeek considered that the amount of dissociation, i.e. number of ions having mobilities approaching that of the bulk value when electrolyte is added, increases with increasing salt concentration.

Deshpande and Marshall (1959, 1961) determined the salt activity, cation activity, and both low and high frequency conductance on K^+ and Ca^{++} Wyoming bentonite systems. Their results indicated that the cations in the diffuse part of the double layer have normal

TABLE 3

APPARENT CONCENTRATIONS OF DISSOCIATED Na IONS AND APPARENT DEGREES OF DISSOCIATION OF Na-BENTONITE (DAVIS, 1942)

Total Na in Suspension	Apparent Concentration of Dissociated Na	Apparent Degree of Dissociation of Na-Bentonite*
meq./l.	meq./l.	per cent
5.199	0.157	3.12
6.103	0.214	4.26
15.15	1.213	24.08

* Based on replaceable Na content of 5.025 meq./l.

mobilities, indistinguishable from those of the salt ions, whereas those in the adsorbed region have zero mobility in d.c. conductance and normal mobility at high frequencies. Chemically adsorbed ions showing neither activity nor conductance were also considered to be present in both systems. van Olphen (1954) concluded that the electrical double layer is not fully expanded into a diffuse counterion atmosphere because the majority of the counterions are located in an adsorbed layer, by a specific adsorption potential. Thus although it would be difficult for a bound sodium ion to move away from the surface, electrophoretic and surface conductance measurements of van Olphen (1957) indicate that it could move relatively easily along the surface.

Thus, there is considerable evidence supporting the view that counterions may be highly associated on both clay mineral and polyelectrolyte surfaces. These associated ions are held in the adsorbed layer with a marked loss in mobility, particularly in the direction normal to the surface. Overbeek (1956) considered that this loss in mobility occurred because of the high electrical potential around the particles at low electrolyte concentrations.

It seems reasonable to suppose that the same type of binding will occur on both surfaces, and that it will be largely electrostatic in origin. Thus, both Fuoss and Bjerrum type ion-pairs equivalent to binding in the I.H.P. and O.H.P. respectively may be considered to occur in both systems. Posner and Quirk (1964) demonstrated that entry of electrolyte ions into the surface regions of montmorillonite and illite is controlled by the need for the electrolyte ions to undergo suitable ion pairing. The free energy of penetration of an electrolyte into the adsorbed water was shown to increase with decreasing hydration. Thus, for example adsorption of water onto illite from caesium chloride solutions did not occur, because all the exchangeable caesium ions were strongly associated, probably as Fuoss type ion pairs.

D. Recent Models of Ion Adsorption.

The models of the adsorbed region discussed so far have involved the concept that the sites of the charge are adsorbed ions, which still possess thermal energy. This is the situation on the classical mercury surface, where the charge arises from the adsorption of ions at the interface. However, where the charge is completely fixed in the structure, as in the clay minerals, there is no possibility of any movement in the charged site. This fixed charge may be balanced by an ion bound at the site or by one of the excess cations in the diffuse layer regions.

The mean potential at any point in the I.H.P. has been considered in such a way that no ion is permanently located at this point. Therefore, when an ion is bound, the mean charge distribution in the I.H.P. around such an ion can no longer be considered homogeneous, but will be given by some function $\sigma(r)$ where r is the distance from the specified adsorbed ion to an arbitrary point on the I.H.P. A diagrammatic illustration of this distribution is presented in Fig. 6. This shows that the problem resolves itself into distinguishing between the mean electrostatic potential at any point in the I.H.P. and the mean potential at the centre of an adsorbed ion occupying this point. Levine, Bell and Calvert (1962) proposed that the difference between these two potentials originated in the discreteness of charge effect, which had been investigated by the Russian scientists Esin and Shikov (1943), Ershler (1946), and Levich, Kiryanov and Filinovsky (1960). Grahame (1958) also considered this effect.

Levine, Bell and Calvert (1962) considered that there were two terms in the perturbation potential of an adsorbed ion. The first is the ordinary electrostatic image term in the wall of the colloidal plate and the second is due to the departure of the surface charge density on the I.H.P. from the otherwise uniform value. A number of approximations to a determination of σ (r) have been suggested. Esin and Shikov (1943) used a model based on a layer of oriented cation-anion pairs, while Ershler (1946) replaced the distribution σ (r) and its image in the charged surface by an infinite hexagonal array of discrete ionic charges in the I.H.P., surrounded on the solution side by an atmosphere of oppositely charged ions. Levine, Bell and Calvert (1962) employed a similar method to the Russian workers which has been termed the "cut-off approximation". They considered that each adsorbed ion is the centre of a circular area of radius r_c (Fig. 6) from which the uniform charge density is

Charge distribution in the I.H.P. surrounding an adsorbed cation using Levine, Bell and Calvert's (1962) cutoff approximation.

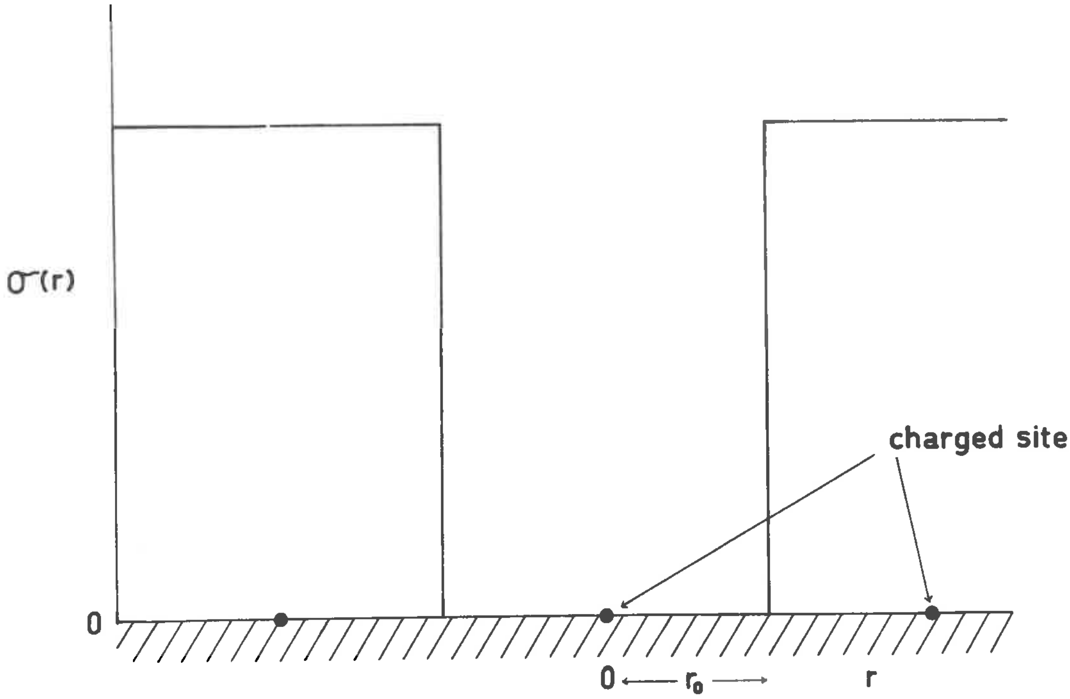


FIGURE 6.

completely removed. This discrete charge effect leads to a new term in the energy of an adsorbed ion, which Levine et al. (1962) showed is very nearly proportional to the concentration of these ions immediately adjacent to the surface, and which had previously been included in the somewhat ill-defined specific adsorption potential of Stern (1924). Levine, Bell and Calvert (1961) and Levine and Bell (1963) incorporated the discrete-charge effect into the colloid stability theory of Derjaguin and Landau (1941) and Verwey and Overbeek (1947). This provided an explanation for a number of phenomena which had been at variance with the stability theory, e.g. the dependence of coagulating electrolyte concentration on the surface potential of colloidal particles. Thus Levine, Bell and Calvert (1961) were able to explain the flocculation behaviour of silver halide sols observed by Kruyt and Klompe (1943) and Tezak, Matijevic and Schulz (1951).

E. The Importance of Dielectric Constant in Double Layer Theories.

In the simple Gouy-Chapman diffuse double layer theory, the ions have been treated as point charges distributed in a dispersion medium of dielectric constant ϵ. This approximation is quite valid for ions in the diffuse part of the double layer although they possess complete hydration sheaths, and thus move as a hydrated entity through the medium of bulk dielectric constant ϵ. However, the macroscopic value of ϵ cannot be used near a charged surface, where the first layer of polar solvent molecules will be highly ordered. In fact, the water structure at a charged surface will be expected to resemble that in the hydration sheath about an ion.

The now generally accepted concept of the variation of the microscopic dielectric constant about an ion may be attributed to Ritson and Hasted (1948). Using two different approaches, one based on Onsager's (1936) expression for dielectric constant, and the other based on Kirkwood's (1939) extension of Onsager's theory, they obtained the following model of the dielectric constant around an ion. A region of complete dielectric saturation exists in the first layer of water molecules around the ion. Here, the dielectric constant has a value of 4 or 5 (Ritson and Hasted, 1948) arising from electron and atom polarization only. The dielectric constant then rapidly increases over the next 2 Å to its ordinary macroscopic value. For monovalent ions the region of dielectric saturation is confined to the first layer of water molecules around an ion. Webb (1926) suggested that the dielectric constant of water in a high intensity electric field was considerably lower than its macroscopic value, owing to orientation and induced polarization effects, while Collie, Hasted and Ritson (1948) showed that the macroscopic dielectric constant falls linearly with increase in ionic strength. Application of the Ritson and Hasted concepts suggests that the dielectric constant in the adsorbed layer should be considerably less than that in the bulk solution, and also in the diffuse layer as was suggested by Conway, Bockris and Ammar (1951). Consideration of the distance of separation of ions in electrolyte solutions of known concentration (Table 4) further supports these suggestions.

The actual value of the dielectric constant in the adsorbed layer is still a source of great interest to surface chemists. The work of Parsons (1961) on the dependence of surface pressure on charge for adsorbed thiourea, of Devanathan (1961, 1962) on the dependence of surface pressure on charge for thiourea and amyl alcohol is consistent with a dielectric constant of 6 to 7 for water in contact with the electrode. Rampolla, Miller and Smyth (1959) obtained a value of 6 for water measured in the microwave region at high frequency.

Although the structure of water in the region immediately adjacent to a charged surface is still a source of considerable controversy (Low (1961), Martin (1960)), it seems reasonable to assume a value of about 6 for the dielectric constant of the primary water layer adsorbed on a clay mineral surface, irrespective of the mechanism of interaction. In fact, the solution to the understanding of the region immediately adjacent to a charged surface, will probably depend for its ultimate analysis on the properties of the ions in the adsorbed layer, the water structure in this layer, allied with knowledge of the forces operating in the complete double layer.

IV. ELECTROSTATIC ENERGY OF ATTRACTION AND IMAGE FORCES.

A. Introduction.

Schofield's equations for film thickness and negative adsorption of chloride agree reasonably well with experiment (Schofield 1946, 1947), suggesting that reliance can be placed on the calculated

TABLE 4

Average Separation of Ions in Solution of a 1:1 Electrolyte

(after Robinson and Stokes, 1955.)

concn. meq./ml.	0.001	0.01	0.1	1.0	10.0
Separation Å	94	44	20	9.4	4.4
ϵ^{*}_{NaCl}	80	80	79	69	-

* Macroscopic dielectric constants calculated using the relationship $\epsilon = \epsilon_{H_2O} + 2\bar{\delta}\, C_o$ (Collie, Hasted and Ritson, 1948). $2\bar{\delta}$ is the molar depression of the dielectric constant.

It is of interest to note that for montmorillonite the charge density is such that if all the exchangeable ions were in the Stern layer, the average separation of monovalent ions would be 12 Å. For illites, the separation would be about 7.7 Å.

double layer repulsive forces. However, the origin and magnitude of the attractive forces, particularly for close distances of approach have been a source of considerable controversy.

The attractive forces between sodium montmorillonite platelets calculated by Norrish (1954) and again by Quirk (1962) using the London-van der Waal's equation

$$F_A = \frac{A}{24\pi}\left\{\frac{1}{D^3} + \frac{1}{(D+\Delta)^3} - \frac{2}{(D+\Delta/2)^3}\right\} \text{dynes/cm}^2 \quad (48)$$

where A = Hamaker constant (Hamaker, 1937)

2D = plate separation

Δ = plate thickness

are presented in Table 5. Until recently there has been a lack of agreement on the value of the Hamaker constant, which is now accepted as being about 5×10^{-14} ergs (Derjaguin et al., 1954; Kitchener and Prosser, 1957). For further discussion on this point see Appendix II.

However, even if the largest measured value of the Hamaker constant (Overbeek and Sparnaay, 1951, 1952, 1954) is used, the lack of agreement between the calculated double layer repulsive force and the London-van der Waal's attractive forces suggests that some other origin for the attractive force is necessary for close distances of approach. In this regard, the treatment of the region close to a charged surface by the method of electrical images seems to offer outstanding possibilities.

B. Interaction Between Ions and Surfaces.

Norrish (1954) considered the electrostatic energy of attraction between an ion and an oppositely charged surface as a compromise between a point charge relationship with $E_A = \frac{\sigma v e}{2d\varepsilon}$ and a condenser relationship with $E_A = \frac{2\pi\sigma^2 d}{\varepsilon}$.

Jordine, Bodman and Gold (1962) used Kelvin's method of electrical images as developed by Maxwell (1891) and Jeans (1908) to develop a general theory of the electrostatic energy of attraction between an ion and an oppositely charged surface. Jeans used the method of images to find the field produced by point charges when half of the field is occupied by a second dielectric. A schematic representation of the situation is shown in Fig. 7, where a point charge e' = ve is placed at the position P', in a medium of dielectric constant ε_w, (e.g. water) to the left of the Z-axis. Let the dielectric constant of the medium to the right of the Z-axis be ε_m. It is proposed to show that the field in the medium ε_w is the same as that due to a charge e' at P' and a certain charge e" at P", the image of P', while the field in the medium ε_m is the same as that due to a certain charge e''' at P' if the whole field was occupied by the medium of dielectric constant ε_w. The potential at some point (x, y, z) due to e' and e'' in water is given by

$$V_w = \frac{e'}{\varepsilon_w\sqrt{(x+d)^2 + y^2 + z^2}} + \frac{e''}{\varepsilon_w\sqrt{(x-d)^2 + y^2 + z^2}} \qquad (49)$$

Image force acting on an ion near a charged surface, separating two media of different dielectric constant.

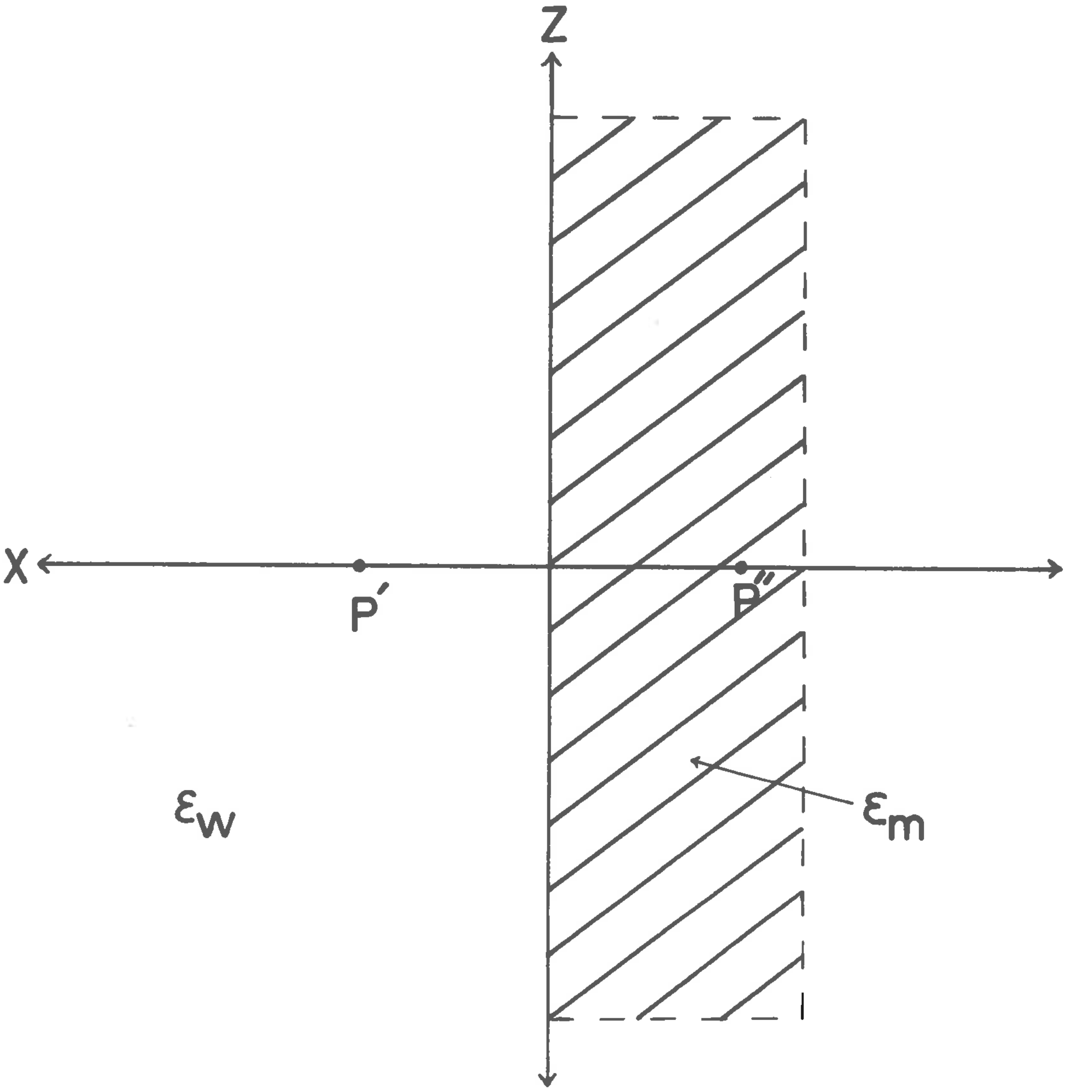


FIGURE 7.

TABLE 5

Comparison of Attractive and Repulsive Forces between Montmorillonite Lamellae

Concn. meq./ml.	Plate Separation Å	Repulsive Force P dynes/cm^2 x 10^{-5}	Attractive Force F_A dynes/cm^2 x 10^{-5}	
			A = 10^{-12}	A = 5×10^{-14}
0.25	34	28.7	9.1	0.45
0.063	57	11.6	1.0	0.05
0.028	79	6.12	0.23	0.01
0.0156	102	3.86	0.074	0.007
0.0100	125	2.59	0.029	0.0015
0.0069	148	2.04	0.013	0.0006

A = 10^{-12} Overbeek and Sparnaay (1951, 1952, 1954)

A = 5×10^{-14} Derjaguin et al. (1951, 1953, 1954)
Kitchener and Prosser (1957)

where (-d,o,o) and (d,o,o) are the co-ordinates of the charges e' and e'' respectively. The potential in the medium of dielectric constant ϵ_m is given by

$$V_m = \frac{e'''}{\varepsilon_w \sqrt{(x+d)^2 + y^2 + z^2}} \tag{50}$$

At a point (o, y, z) on the boundary,

$$V_w = \frac{e' + e''}{\varepsilon_w \sqrt{d^2 + y^2 + z^2}} \tag{51}$$

and

$$V_m = \frac{e'''}{\varepsilon_w \sqrt{d^2 + y^2 + z^2}} \tag{52}$$

The condition that the potential at each point in the boundary shall be continuous, is satisfied by taking

$$e' + e'' = e''' \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \tag{53}$$

A secondary boundary condition is given by the application of Gauss' theorem to unit area of the surface which separates two media of different dielectric constant. This condition, due to the discontinuity in the normal component of the displacement is

$$\varepsilon_w \frac{\partial V_w}{\partial n_w} + \varepsilon_m \frac{\partial V_m}{\partial n_m} = -4\pi\sigma \tag{54}$$

where n_w is the normal drawn from the boundary into the water, n_m the normal into the other medium, and σ the surface density of charge. If the normal coincides with the X-axis, equation (54) becomes

$$-\varepsilon_w \frac{\partial V_w}{\partial x} + \varepsilon_m \frac{\partial V_m}{\partial x} = -4\pi\sigma \tag{55}$$

At the point (o, o, o) on the boundary

$$\varepsilon_w \frac{\partial V_m}{\partial x} = -\frac{e'''}{d^2} \tag{56}$$

and

$$\varepsilon_w \frac{\partial V_w}{\partial x} = -\frac{e'}{d^2} + \frac{e''}{d^2} \tag{57}$$

Thus the second boundary condition becomes

$$\varepsilon_w(e''-e') + \varepsilon_m e''' = \varepsilon_w \cdot 4\pi\sigma d^2 \tag{58}$$

Jordine, Bodman and Gold (1962) satisfied the boundary conditions by putting

$$e'' = \frac{(\varepsilon_w - \varepsilon_m)e'}{\varepsilon_w + \varepsilon_m} + \frac{\varepsilon_w \cdot 4\pi\sigma d^2}{\varepsilon_w + \varepsilon_m} \tag{59}$$

and

$$e''' = \frac{\varepsilon_w \cdot 2e'}{\varepsilon_w + \varepsilon_m} + \frac{\varepsilon_w \cdot 4\pi\sigma d^2}{\varepsilon_w + \varepsilon_m} \tag{60}$$

The force exerted on the medium by the ion in water is then given by

$$\frac{e'e''}{\varepsilon_w(p'p'')^2} = \frac{(\varepsilon_w - \varepsilon_m)(e')^2}{\varepsilon_w(\varepsilon_w + \varepsilon_m)4d^2} + \frac{\pi\sigma e'}{(\varepsilon_w + \varepsilon_m)} \tag{61}$$

Substituting ve for e' gives

$$\frac{e'e''}{\varepsilon_w(P'P'')^2} = \frac{(\varepsilon_w - \varepsilon_m)v^2e^2}{\varepsilon_w(\varepsilon_w+\varepsilon_m)4d^2} + \frac{\pi\sigma v e}{(\varepsilon_w+\varepsilon_m)} \qquad (62)$$

and the electrostatic energy of attraction is

$$E_A = \frac{(\varepsilon_w - \varepsilon_m)v^2e^2}{\varepsilon_w(\varepsilon_w+\varepsilon_m)2d} + \frac{2\pi\sigma v e d}{(\varepsilon_w+\varepsilon_m)} \qquad (63)$$

Jordine (1963) showed that Norrish's (1954) suggestion of a compromise between a point charge and condenser relation was correct in principle by expressing the electrostatic energy of attraction in units of energy per cm^2. This was done by multiplying the right hand side of equation (63) by the number of ions per cm^2 (i.e. $\frac{\sigma}{ve}$). The relationship obtained is

$$E_A = \frac{(\varepsilon_w - \varepsilon_m)\sigma v e}{\varepsilon_w(\varepsilon_w+\varepsilon_m)2d} - \frac{2\pi\sigma^2 d}{(\varepsilon_w+\varepsilon_m)} \text{ ergs/cm}^2. \qquad (64)$$

These terms are in effect the point charge relationship and the condenser relationship proposed by Norrish. Consideration of equations (63) and (64) shows that the sign of E_A depends on the difference in the dielectric constants. If $\varepsilon_w > \varepsilon_m$, E_A is positive, while if $\varepsilon_w < \varepsilon_m$, E_A is negative.

The relationship derived above is essentially the nett interaction between an ion and an oppositely charged surface, van der Waal's attractive forces being neglected. Since, for the general case of a negatively charged surface when $\varepsilon_w > \varepsilon_m$, the image term gives rise to a nett repulsion, and the condenser term to an attraction, the nett energy fromthe summation of the two forces may be considered to represent the total potential energy of an ion adjacent to the charged surface. Calculations show that the nett energy can change from a repulsive to an attractive energy with increasing distance from the negatively charged surface.

The method of electrical images employed in the above derivation of the nett electrostatic energy was also applied to the negative adsorption of ions at the air-water interface by Wagner (1924) and Onsager and Samaras (1934). Ershler (1946), Grahame (1958) and Levine, Bell and Calvert (1961) also used image concepts in developing their discreteness of charge theories in the inner region of the double layer. Posner and Quirk (1964) also used image force concepts to explain the adsorption of water from concentrated electrolyte solutions by clay mineral surfaces.

C. Total Interaction Between Charged Surfaces.

The theory of the electrostatic attraction between an ion and an oppositely charged surface may be extended to the case of interaction between opposed parallel charged plates. Jordine, Bodman and Gold (1962) developed the theory for a point charge e' = ve/2. The derivation is exactly the same, until the substitution for e' is made in equation (45). The electrostatic energy of attraction between a plate and an interlayer cation then becomes

$$E_A = \frac{(\varepsilon_w - \varepsilon_m)v^2e^2}{\varepsilon_w(\varepsilon_w + \varepsilon_m)8d} + \frac{\pi\sigma ved}{(\varepsilon_w + \varepsilon_m)} \qquad (65)$$

The energy of interaction between two opposed plates is then obtained by multiplying the right hand side of equation (65) by $-\frac{2\sigma}{\upsilon e}$, that is the number of ions per cm^2. Equation (65) then becomes

$$E_A = \frac{-(\varepsilon_w - \varepsilon_m)\sigma \upsilon e}{\varepsilon_w(\varepsilon_w + \varepsilon_m) 4d} - \frac{2\pi\sigma^2 d}{(\varepsilon_w + \varepsilon_m)} \text{ ergs/cm}^2 \qquad (66)$$

This equation represents the total interaction energy between two opposed planar charged surfaces and the interlayer ions in relation to the distance of separation. (2d).

Jordine (1963) calculated the total attraction energy for montmorillonite with a charge density $\sigma = -3 \times 10^4$ e.s.u. per cm^2, $\epsilon_w = 80$, and $\epsilon_m = 2$. He showed there was a large nett repulsive force close to the surface, becoming a nett attractive force for $d > 2.5$ Å. Thus using the macroscopic dielectric constant for water there is a nett attraction over the entire range of plate separations between 5 Å and 20 Å, the upper limit being set by the fact that the plate thickness is < 10 Å. Jordine, Bodman and Gold (1962) considered that the macroscopic dielectric constant was not accurate enough in the region close to the surface, because of electrical saturation effects. They calculated the arithmetic average of the values of ϵ_w at the surface of the ion and the values over some distance, d, from the ion, using Debye's (1929) concepts. Jordine (1962) obtained an energy well in the neighbourhood of d = 4 Å, equivalent to an X-ray spacing of about 18 Å. The van der Waal's-London energy of attraction (V_A) was also calculated, and shown to be swamped over the entire region in which the electrostatic image theory is valid. Furthermore, double layer forces of repulsion probably take over within a distance of 15 Å from the surface (plate separations of 30 Å).

V. CLAY MINERALS.

A. Structure.

The elucidation of the atomic structure of mica by Pauling (1930) together with the advent of X-ray diffraction analysis (Hendricks and Fry, 1930; Ross and Kerr, 1931; Kelley, Dore and Brown, 1931) provided the foundation for the derivation of the crystalline structure of the clay minerals. Since then, a particularly voluminous literature has arisen; excellent general reviews have been written by Marshall (1949) and Grim (1953).

The layer lattice clay minerals are composed of two basic structural units. The first consists of two sheets of loosely packed oxygens or hydroxyls in which aluminium, iron or magnesium atoms are embedded between the sheets in octahedral co-ordination with the oxygen and hydroxyl groups. The second unit is built up of silica tetrahedra arranged in a hexagonal network, with the tips of the tetrahedra all pointing in the same direction with their bases all in the same plane. The clay minerals fall into two groups:- the diphormic, kaolin or 1:1 lattice group in which one silica and one alumina sheet combine to form the lattice, and the triphormic or 2:1 lattice group consisting of two silica tetrahedral sheets with a central octahedral sheet. The general structure of the 2:1 lattice minerals may be represented by the uncharged pyrophyllite structure shown in Fig. 8.

B. Origin of Charges.

On considering the structural interpretation of chemical analyses of clay minerals, Marshall (1935) concluded, and later Hendricks (1942) emphasized that the principal charge on the triphormic minerals arises through isomorphous substitution in either (or both) the octahedral or tetrahedral sheets. The dissociation of H from -SiOH groups is only important at high pH values.

The charge deficiency in the mica group of minerals arises through the replacement of about one-quarter of the tetrahedral silicon atoms by aluminium atoms (Table 6). The charge is balanced by potassium ions, which just fit into holes in the surface oxygen layers. The illite clay minerals, which like muscovite possess non-expanding crystal lattices, are characterized by a substitution of only about one-sixth of the tetrahedral silicon by aluminium. Brown and Norrish (1952) considered that the charge deficiency is balanced by non-exchangeable potassium and oxonium (H_3O^+) ions which provide strong electrostatic attractive forces, between adjacent sheets, such that water and other polar solvents cannot enter between the sheets and cause lattice expansion. The only exchangeable cations are those associated with charged sites on the external surfaces of mica-like clay crystals.

The expanding lattice or montmorillonite group of clay minerals possess considerably less charge than the illite minerals.

Structure of pyrophyllite (schematic).

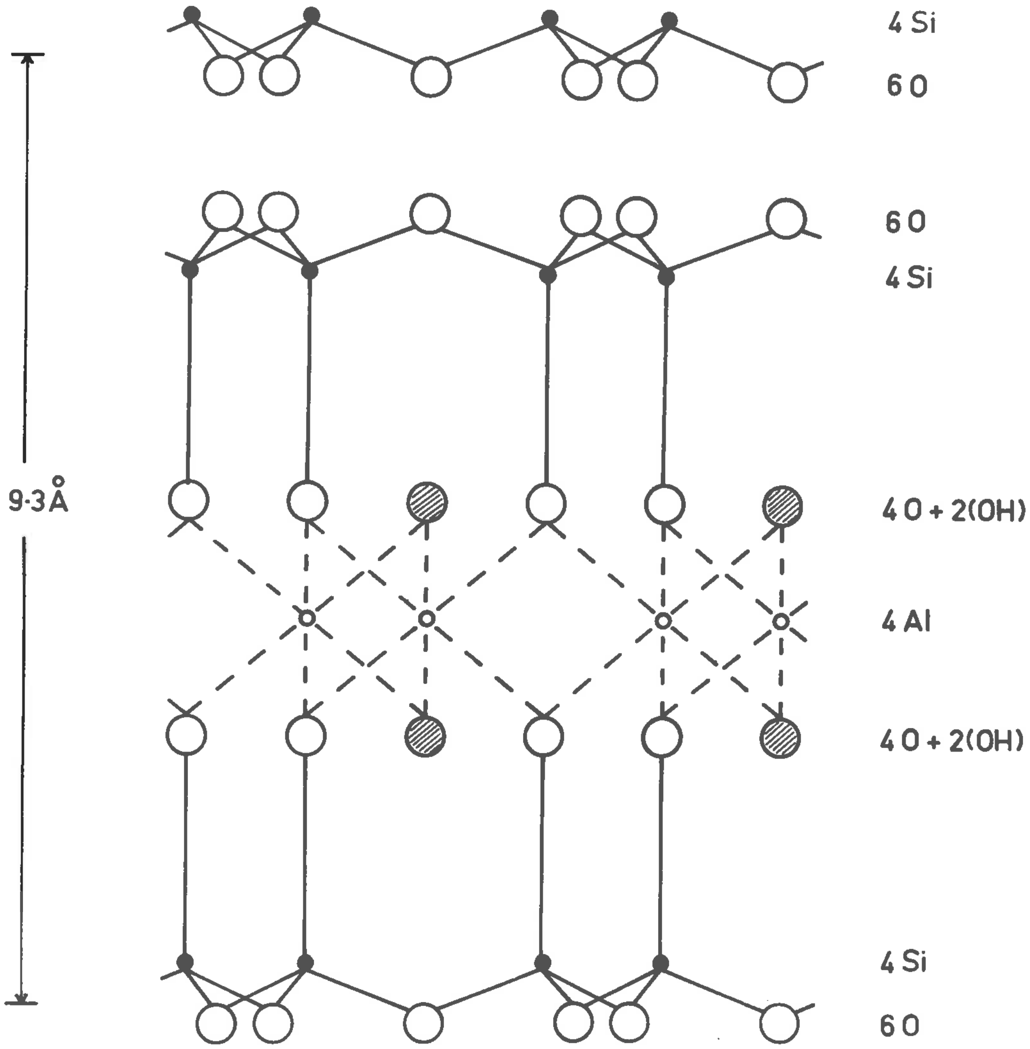


FIGURE 8.

The charge of the various members of the montmorillonite group may arise through substitution in either the octahedral or tetrahedral layers (Table 6, Ross and Hendricks, 1945). The charge in montmorillonite itself arises in the octahedral layer, while that in saponite arises from the substitution of aluminium for silicon in the tetrahedral layer.

The charge deficiency in the montmorillonite group of clay minerals is balanced by exchangeable cations situated between the silicate layers. Hofman, Endell and Wilm (1933) demonstrated that adsorption of water by montmorillonite was accompanied by an increase in the c-axis spacing, and suggested that the water entered between the individual silicate sheets. Hendricks, Nelson and Alexander (1940) and later MacKenzie (1950) showed that the first water to enter the interlayer spacing was due to ion hydration, after which the water layers build up in a stepwise manner (Bradley, Grim and Clark, 1937) to a d(001) X-ray spacing of about 19 Å (occasionally 22.5 Å). Norrish (1954) confirmed that crystalline swelling is dependent on the hydration energy of the interlayer cation, and showed that the maximum crystalline swelling of the triphormic 2:1 lattice minerals decreased with increasing charge density (Table 7). The repulsive forces involved in limited crystalline swelling of divalent ion systems cannot be attributed to the interaction of diffuse double layers between plates, because the basal spacing remains at about 19 Å over the concentration range from molar to distilled water , (Norrish and Quirk, 1954).

TABLE 6

FORMULAE FOR SOME MEMBERS OF THE MONTMORILLONITE GROUP SUGGESTED BY ROSS AND HENDRICKS (1945)

	Dioctahedral montmorillonites
Montmorillonite	$(OH)_4\ Si_8\ (Al_{3.34}\ \underset{\substack{\downarrow \\ Na_{o.66}}}{Mg_{0.66}})\ O_{20}$
Beidellite	$(OH)_4\ (Si_{6.34}\ \underset{\substack{\downarrow \\ Na_{0.66}}}{Al_{1.66}})\ Al_{4.34}\ O_{20}$
Nontronite	$(OH)_4\ (Si_{7.34}\ \underset{\substack{\downarrow \\ Na_{0.66}}}{Al_{0.66}})\ Fe_4\ O_{20}$
	Trioctahedral montmorillonites
Hectorite	$(OH)_4\ Si_8\ (Mg_{5.34}\ \underset{\substack{\downarrow \\ Na_{0.66}}}{Li_{0.66}})\ O_{20}$
Saponite	$(OH)_4\ Si_{7.34}\ \underset{\substack{\downarrow \\ Na_{0.66}}}{Al_{0.66}})\ Mg_6\ O_{20}$
Muscovite	$(OH)_4\ (Si_6\ \underset{\substack{\downarrow \\ K_{2.0}}}{Al_{2.0}})\ Al_4\ O_{20}$
Biotite	$(OH)_4\ (Si_6\ \underset{\substack{\downarrow \\ K_{2.0}}}{Al_{2.0}})\ (Mg.Fe)_6\ O_{20}$
Margarite	$(OH)_4\ (Si_{4.0}\ \underset{\substack{\downarrow \\ (\underline{Ca})_{4.0} \\ 2}}{Al_{4.0}})\ Al_4 \cdot O_{20}$
Illite (approximate)	$(OH)_4\ (Si_{6.67}\ \underset{\substack{\downarrow \\ K_{1.33}}}{Al_{1.33}})\ Al_4 \cdot O_{20}$

TABLE 7

GENERAL PROPERTIES OF THE 2:1 LATTICE ALUMINOSILICATES

Mineral	Isomorphous Replacement meq./100 g.	Total area m^2/g.	Charge density esu/cm^2	d(001) spacing		
				Na^+	K^+	Mg^{++}
Pyrophyllite	0	0	0	9.3	9.3	9.3
Montmorillonite	90-110	700	3.8×10^4	$19(\longrightarrow)$	$15(\dashrightarrow)$	19
Vermiculite	130-150	700	6×10^4	14.8	11	14.6
Muscovite	250	(700)	10^5	14.3	10	14.3
Illite	200	100	8×10^4	10	10	10
Margarite	500	-	2×10^5	-	-	-

In contrast to the behaviour of the divalent ion systems, Li^+ and Na^+ montmorillonite at electrolyte concentrations less than about 0.6 N and 0.3 N respectively, give extensive crystalline swelling (Norrish and Quirk, 1954), with the plate separation increasing in a manner inversely proportional to the square root of the electrolyte concentration (Norrish, 1954). This type of swelling is due to diffuse double layer formation on the clay mineral surfaces.

Aylmore and Quirk (1959) have observed that swelling taking place between crystals of Ca^{++} Willalooka illite is not sensitive to change in electrolyte concentration between molar and distilled water. This was the basis on which Aylmore and Quirk postulated the presence of domains. Further, it suggests that there is a basic similarity between the limited crystalline swelling of Ca^{++} montmorillonite and the inter-crystalline swelling of an illite. Posner andQuirk (1964) have shown for concentrated electrolyte solutions, a marked similarity between the adsorption of water on illite with predominandy external surfaces, and montmorillonite with predominantly internal surfaces. This "indicates that the adsorption of two layers of water provides the bulk of the energy of inter-crystalline swelling which is common to all clays". These measurements highlight the statement (Aylmore and Quirk, 1959; Quirk and Aylmore, 1960; Edwards and Quirk, 1962) that the central problem in interpreting the mechanical behaviour of clay-water systems is to distinguish between water which is simply enmeshed in a gel structure, and water directly associated with clay surfaces. In these circumstances it is felt that more extensive measurements of chloride exclusion particularly in dilute solutions would help to resolve the problem of distinguishing between gel water and diffuse double layer water.

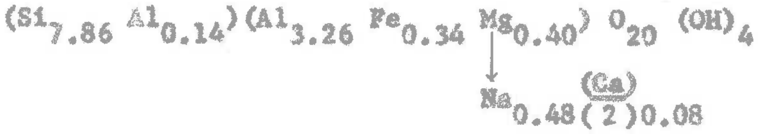
2. EXPERIMENTAL MATERIALS AND METHODS.

I. DESCRIPTION OF CLAY MATERIALS.

Most of the experimental data to be presented and discussed involves the following three clay minerals:-

(1) Fithian illite, obtained from Ward's Natural Science Establishment Inc., and is Illite No. 35 of the American Petroleum Institute's Research Project No. 49 (1951). No crystalline impurities in appreciable amounts were detectable by X-ray diffraction. Greenland and Quirk (1962) reported a surface area of 96 m^2/g. from cetyl-pyridinium bromide adsorption, which agreed very closely with the nitrogen surface area of 93 m^2/g. This indicates that Fithian illite is completely free of any expanding lattice material.

(2) Montmorillonite (Wyoming bentonite) - obtained from Ward's Natural Science Establishment Inc. This mineral, from the John C. Lane Tract, Upton, Wyoming, is the standard clay mineral number 25b of the A.P.I. Research Project No. 49. Chemical analysis reveals that it has the composition



$$(Si_{7.86}\,Al_{0.14})(Al_{3.26}\,Fe_{0.34}\,\underset{\substack{\downarrow\\ Na_{0.48}\left(\frac{Ca}{2}\right)_{0.08}}}{Mg_{0.40}})\,O_{20}\,(OH)_4$$

Analysis by X-ray diffraction has shown the clay to be mineralogically pure except for about 3% quartz.

(3) Grundite illite, from County Grundy, Illinois, obtained from Illinois Clay Products Co., Joliet, Illinois. X-ray diffraction analysis indicated < 3% quartz was present as an impurity. Molloy and Kerr (1961) first drew attention to the asymmetry of the 10 Å basal reflection and suggested the clay may be interlayered with expanding lattice material. This is in agreement with the ideas of Hendricks and Alexander (1939) who suggested Grundite illite should be classed as a mixed illite-montmorillonite structure. Greenland and Quirk (1962) demonstrated Grundite illite is an interstratified mineral, when they obtained a surface area of 161 m^2/g. from cetyl-pyridinium bromide adsorption, compared with an area of 105 m^2/g. from low temperature nitrogen adsorption.

In addition, chloride exclusion experiments were also conducted on a few homoionic samples of the following materials:-

(1) Milford saponite, from Milford, Utah. This material was kindly supplied by Dr. K. Norrish, Clay Mineralogy Section, C.S.I.R.O. Division of Soils, Adelaide. X-ray examination showed this sample was very pure mineralogically. Chemical analysis (Norrish, unpublished) reveals that it has the following composition.

$$(Si_{7.64}\ \underset{\substack{\big\downarrow \\ \frac{Ca}{2}\ 0.83}}{Al_{0.36}})(Mg_{5.52}\ Al_{0.20}\ Fe_{0.08})\ O_{20}\ (OH)_4$$

Saponite is thus a trioctahedral magnesium montmorillonite, possessing a nett negative charge which is tetrahedral in origin.

(2) Silica powder - this has a nitrogen surface area of 155 m^2/g.

II. PREPARATION OF HOMO-IONIC CLAY SUSPENSIONS.

The natural clay minerals were dispersed in distilled water after sodium saturation where necessary. The < 2μ equivalent spherical diameter fraction was separated by sedimentation under gravity. Solid NaCl was then added to flocculate the < 2μ clay fraction. Where necessary, a calculated amount of 10^{-2}N HCl was added to the flocculated suspension to remove any calcium carbonate present. Repeated washing and centrifuging using molar NaCl containing 10^{-3}N HCl was then used to wash the clay suspension to a final equilibrium pH approaching 3.0. This equilibrium condition was also characterized by a constant rate of release of aluminium, which was determined by the Alizarin-Red-S method (Bond, 1957). This stage constitutes the standard preparation procedure, with all < 2μ clay fractions being brought to this point before starting to prepare the various homo-ionic clay suspensions. The one exception was Milford saponite which was only washed down to pH 4.0, owing to its greater susceptibility to acid attack.

The standard preparation procedure has been designed to ensure that exchangeable aluminium was reduced to a minimum level. Aluminium liberation from clay lattices during sample preparation has been discussed by Samson (1953), Bolt and Warkentin (1956), Martin (1960), Lin and Coleman (1960) and Coleman and Craig (1961). As a result, the procedure of washing with a molar salt solution at pH 3.0 has been considered optimum (Lin and Coleman, 1960). In the standard preparation procedure, molar NaCl was used to reduce the electrical potential at the surface, thus buffering the acid attack on the clay mineral lattice.

With the exception of rubidium and caesium where 0.1 N solutions were used, the clays prepared by the standard procedure were subjected to repeated washing and centrifuging with 1.0 N solutions of the appropriate chlorides. The procedure involved six washes, including a final overnight equilibration on an end-over-end shaker. The clay suspensions were then washed free of excess salt by repeated washing and centrifuging with glass-distilled water. When the homo-ionic clays started to disperse, removal of salt was completed by transferring the suspensions into "Visking" cellulose casing and dialysing against glass distilled water, until the resistance of the dialysate approached that of the water. About 10 days was usually required, with daily replacement of the dialysate by water.

Most of the experimental work was conducted on the salt free homo-ionic clay suspensions. However, a few experiments were carried out on powders prepared by drying the suspensions at 70°C, and grinding lightly so that the powder passed through a 120 mesh sieve.

III. CHLORIDE EXCLUSION TECHNIQUES.

Aliquots of the particular homo-ionic clay suspension were pipetted into previously weighed polyethylene centrifuge tubes of capacity 40 ml. fitted with push-fit caps. A second weighing was made to obtain the weight of suspension added. A sample of the suspension was oven-dried at 350°C, to determine the percentage of clay in the suspension. Thus the weight of clay added to the reaction tubes could be calculated. Known volumes of the appropriate standard chloride solutions were then pipetted into the reaction tubes. A further weighing was made, to obtain the weight of solution added. The range of equilibrium electrolyte concentrations used generally varied from 0.5 - 0.003 meq./ml.

The reaction tubes were then firmly stoppered and equilibrated for 3 days on an end-over-end shaker in a constant temperature room, maintained at 25°C. Before analysis, the reaction tubes were reweighed, so that any loss in weight could be detected and appropriate minor corrections applied on the basis that water vapour only was lost. The reaction tubes were then centrifuged for 20 minutes at 2,000 g. The supernatant was poured off, and then the tube and contents were reweighed to determine the weight of liquid entrained in the clay.

The chloride content of each phase was determined potentiometrically by titration with standard $AgNO_3$ using a modification of Best's (1929) method which was later modified by Kolthoff and Kuroda (1951). The amount of negative adsorption (chloride exclusion) was calculated from the difference between the amount of chloride per unit weight of suspension and supernatant, divided by the weight of clay in the reaction tube. In many instances the amounts of chloride added were accurately controlled, and hence chloride exclusion could also be calculated simply from the increase in concentration of the supernatant over the expected concentration. Thus an internal check of the experimental results was often possible. The density of the water was assumed to be unity for all solutions, except the higher salt concentrations of the Rb, Cs, Sr and Ba chlorides where the necessary corrections were made. Furthermore, the density of adsorbed water only varies by about 2-3% from that of pure water. (Low, 1958). The overall accuracy of all the results reported in this thesis is ± 3%.

IV. SUBSIDIARY MEASUREMENTS USED IN CHARACTERIZING THE HOMO-IONIC CLAY SYSTEMS.

A. Surface area determinations.

Low temperature nitrogen adsorption was used in conjunction with the B.E.T. theory to determine the surface areas of the various homo-ionic clay materials. Clay cores were formed by compression of the lightly ground powder, equilibrated at a relative vapour pressure of 0.96 (at 20°C) over saturated K_2SO_4 in a vacuum desiccator. The clay was compressed to 1200 atmospheres pressure by means of a hydraulic jack and the cores were then out-gassed at 300°C. The nitrogen adsorption isotherms were carried out in a standard volumetric adsorption apparatus (Culver and Heath, 1954; Aylmore, 1960).

Nitrogen adsorption does not measure intracrystalline surfaces. Thus depending on the amount of internal crystal surfaces available in aqueous suspension, the B.E.T. nitrogen areas will always be less than or equal to the total available area in suspension. Greenland and Quirk (1962) used the adsorption of cetyl-pyridinium bromide from aqueous solution to determine the total surface area, including intra-crystalline surfaces, of the clay minerals with expanding lattices.

CPB adsorption was determined by shaking 0.5 g. samples of the oven-dried (70°C) clay powder withCPB solutions of concentrations between 0.1 and 2.0 per cent at 25°C for 16 hours. The amount of CPB adsorbed was obtained after determining the final concentration of the supernatant from the U.V. absorption of the solution at 259 mμ.

B. X-ray diffraction measurements.

Chloride exclusion from intra-crystalline surfaces of the expanding lattice clay minerals will be very dependent on the plate separations within crystals. X-ray diffraction techniques were used to determine the basal spacings of various homo-ionic montmorillonites and saponites in equilibrium with the appropriate chloride solutions of varying concentration.

Iron-filtered Co radiation obtained from a Phillips PW 1010 X-ray generator was used with a model PW 1050 diffractometer. X-ray diffraction diagrams were obtained from the clay pastes by spreading them as a thin film on a ceramic tile (Kinter and Diamond, 1956). In order to prevent any change in electrolyte concentration by drying, the tile was covered with a thin polythene film.

C. Exchange capacity determination.

Cation exchange capacities of the clay minerals used were determined by saturation of the clay with ammonium by passing a small amount of suspension through a column of the NH_4^+ form of the cation exchange resin Amberlite IR-120 (Cowan and White, 1958). The ammonium content of the effluent slurry was then determined by steam distillation of the ammonium clay suspension with MgO in a Markham still. The ammonia was collected in 5 ml. of 4% boric acid solution and estimated by titration against standard 0.01N HCl using a mixed brom-cresol green-methyl red indicator.

In some instances the exchange capacity was obtained by washing the homo-ionic clay three times with molar ammonium acetate, centrifuging and collecting the washings which were bulked. The cations in the bulk supernatant were then determined. Calcium was determined by titration at pH 10 with the disodium salt of ethylene-diamine tetra-acetic acid, using Eriochrome Black T indicator (Schwarzenbach and Biedermann, 1948; Jackson, 1958). Sodium was determined using an EEL flame photometer.

V. CONTROLLED pH EXPERIMENTS.

Several reports occur in the literature of the variation of charge carried by soils and clay minerals with pH. (Schofield, 1939, 1940, 1949; Cashen, 1959; Fieldes and Schofield, 1960; Quirk, 1960; Bolt, 1960; Cashen, 1961; Frissel, 1961; and de Haan and Bolt, 1963). The origin of the permanent charge in illites and montmorillonites has been shown to be due to isomorphous replacement (see page 59). Fieldes and Schofield (1960) showed that montmorillonite possesses a virtually constant negative charge over the pH range 4-8, in which range most of the experiments to be reported in this thesis were conducted. At higher pH values, increases in negative charge from about 100 meq./100 g. up to 150-160 meq./100 g. have been reported (Russell, 1961). Schofield (1939) suggested that dissociation of H^+ from OH^- groups attached to edge silicon atoms caused the increase in negative charge.

$$- SiOH \rightleftharpoons SiO^- + H^+$$

Negative adsorption is not sensitive to varying negative charge, so that no increases in chloride exclusion would be expected from the increase in negative charge at high pH. However, Schofield and Samson (1953) and later Quirk (1960) showed that positive adsorption of chloride on the edge face of kaolinite could considerably exceed the negative adsorption of chloride ions from the negative cleavage face. For this reason some experiments at controlled pH were designed to investigate the possibility of the existence of positive charges in these systems.

The effect of any variable charge on the exclusion of chloride from Na^+ and Ca^{++} Grundite illites and Ca^{++} Wyoming bentonite was measured in electrolyte solutions of concentration 0.1 and 0.01 meq./ml. The range of pH used varied from 1.5 to 12.0 in the various experiments. Preceding these experiments, complete titration curves were determined on both the Na^+ and Ca^{++} suspensions so that an estimate could be made of the amount of acid (HCl) or alkali (NaOH; $Ca(OH)_2$) required to bring the suspension near to the desired pH.

Duplicate tubes were set up. After equilibrium, one of the replicates was analysed for chloride, while the supernatant from the other was used for pH determination. All pH measurements were made using a glass electrode-calomel system in conjunction with a Cambridge pH meter.

3. RESULTS AND DISCUSSION

I. MONOVALENT ION SYSTEMS

A. Chloride Exclusion by Fithian Illite.

1. General Results.

The results describing the exclusion of chloride from the surface regions of homo-ionic Li^+, Na^+, K^+, NH_4^+, Rb^+ and Cs^+ Fithian illites are presented in Fig. 9. These are plotted in accordance with Schofield's negative adsorption equation (39), i.e. the exclusion volume is plotted against $\frac{q}{\sqrt{z\beta C_o}}$. It may be noted that good straight lines are obtained. At a given electrolyte concentration, the volume of exclusion diminishes in the order Li > Na > K > NH_4 > Rb > Cs, which is the same order as decreasing ion hydration. Surface areas obtained from the slopes of the lines vary, as indicated on Fig. 9, from 80 m^2/g. for the Li system to zero for the Cs system. The surface areas measured by nitrogen adsorption were about 110 m^2/g, and on this basis it would be expected that the chloride exclusion areas should have been of this magnitude, consistent with exclusion from high charge density surfaces of area equal to the low temperature nitrogen area.

CHLORIDE EXCLUSION BY FITHIAN ILLITE

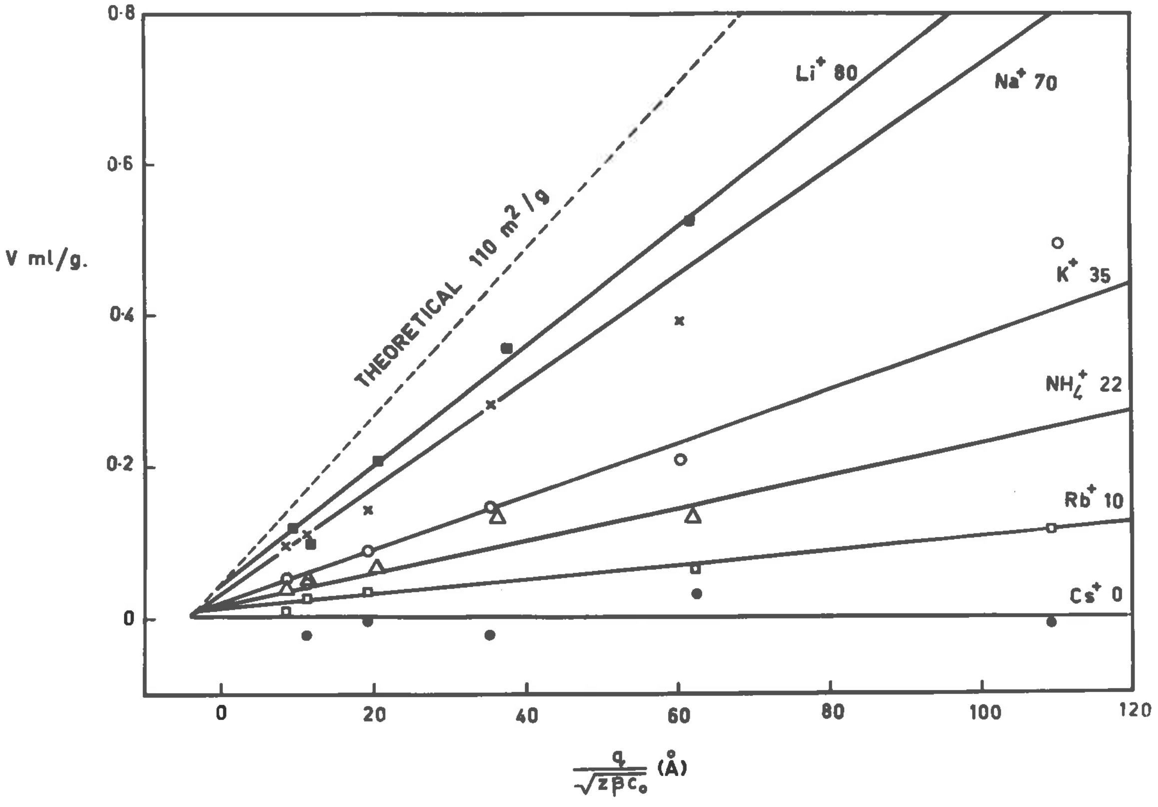


FIGURE 9.

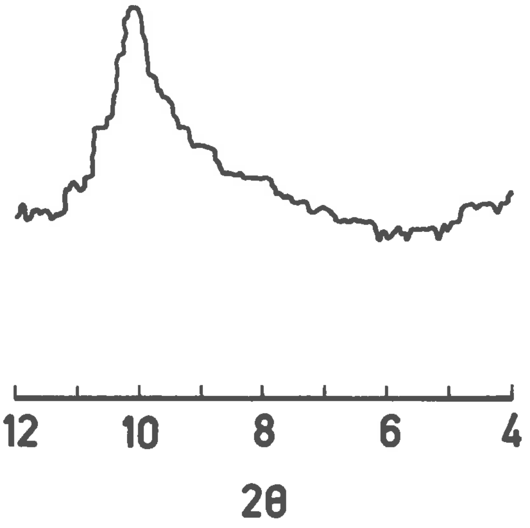
The intercepts of the chloride exclusion plots on the volume axis are seen to diminish as ion size increases and ion hydration decreases. Although diffuse double layer theory will not apply at high concentrations approaching the volume axis, the intercepts give an idea of the relative magnitude of the regions close to the surface from which electrolyte is excluded. At high concentrations, Posner and Quirk (1964) showed the presence of three discontinuities, corresponding to the inability of electrolyte to penetrate into three surface regions until particular concentrations have been exceeded.

A number of possible explanations can be advanced to interpret the reduction in area observed on passing through the alkali metal series from Li to Cs. The possibility of differences in crystal size was rejected on two grounds. Firstly, the general agreement between the nitrogen surface areas of the various homo-ionic illites (Table 8) does not support the suggestion that crystals are condensed together to give larger crystals, and thus a small overall area per unit weight of clay. Further an analysis of X-ray diffractometer tracings on Li and Cs Fithian illite powders for line broadening (Fig. 10) did not indicate any differences in crystal size.

The possibility that the clay crystals approached one another permitting a Donnan equilibrium to govern the distribution was tested using the simple Donnan theory for 1:1 electrolytes in the following form, derived by Posner and Quirk (1964) from Glueckauf and Watts' (1962) treatment, omitting activity coefficients.

X-ray diffractometer tracings of Fithian illite powders.

(a) **Lithium**



(b) **Caesium**

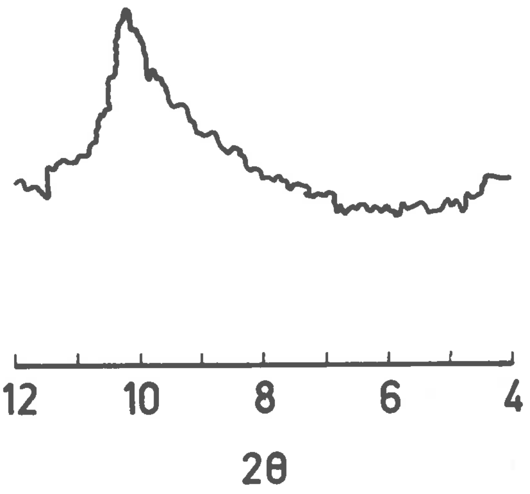


FIGURE 10.

TABLE 8

NITROGEN SURFACE AREAS OF HOMOIONIC FITHIAN ILLITES

Saturating Cation	N_2 area
	$m^2/g.$
Li^+	116
Na^+	109
K^+	113
NH_4^+	118
Rb^+	105
Cs^+	112

$$C_o = \frac{N\ (E - N)}{W\ (E - 2N)} \quad \ldots\ldots\ldots\ldots\ldots \quad (67)$$

where E = exchange capacity of clay in meq./g.

C_o = bulk electrolyte concentration in meq./ml.

N = negative adsorption in meq./g. of clay

W = volume of water per unit weight of clay from which exclusion is taking place.

Assuming that the volume of water from which exclusion occurs is equal to the exclusion volume from 0.01 molar solutions of Li, K, Rb chlorides, the corresponding volumes at other electrolyte concentrations can be calculated. It is quite apparent from Fig. 11 that the Donnan exclusion volumes bear no relationship to the experimental straight lines presented in Fig. 9. It does not appear, therefore, that interactions between double layers associated with adjacent clay crystal surfaces are responsible for the observed reductions in surface area.

The permanent negative charge of the illite due to isomorphous replacement in the tetrahedral layer is balanced by the charge in the Stern layer immediately adjacent to the mineral surface, together with the nett diffuse layer charge due to an excess of cations over anions. It is believed that the reductions in area arise because of binding of exchangeable cations in the Stern layer, with a consequent lowering of the charge density at the Stern-diffuse layer boundary. The amount of ion binding, as measured by chloride exclusion, would seem to increase on passing through the series from Li to Cs. In the later case, all the exchange sites appear to be filled with bound caesium ions.

CALCULATED DONNAN CURVES FOR FITHIAN ILLITE

ACCORDING TO $C_o = \frac{N(E-N)}{W(E-2N)}$ W was taken as exclusion (vol.) from 0·01N solution of Li, K and Rb chlorides

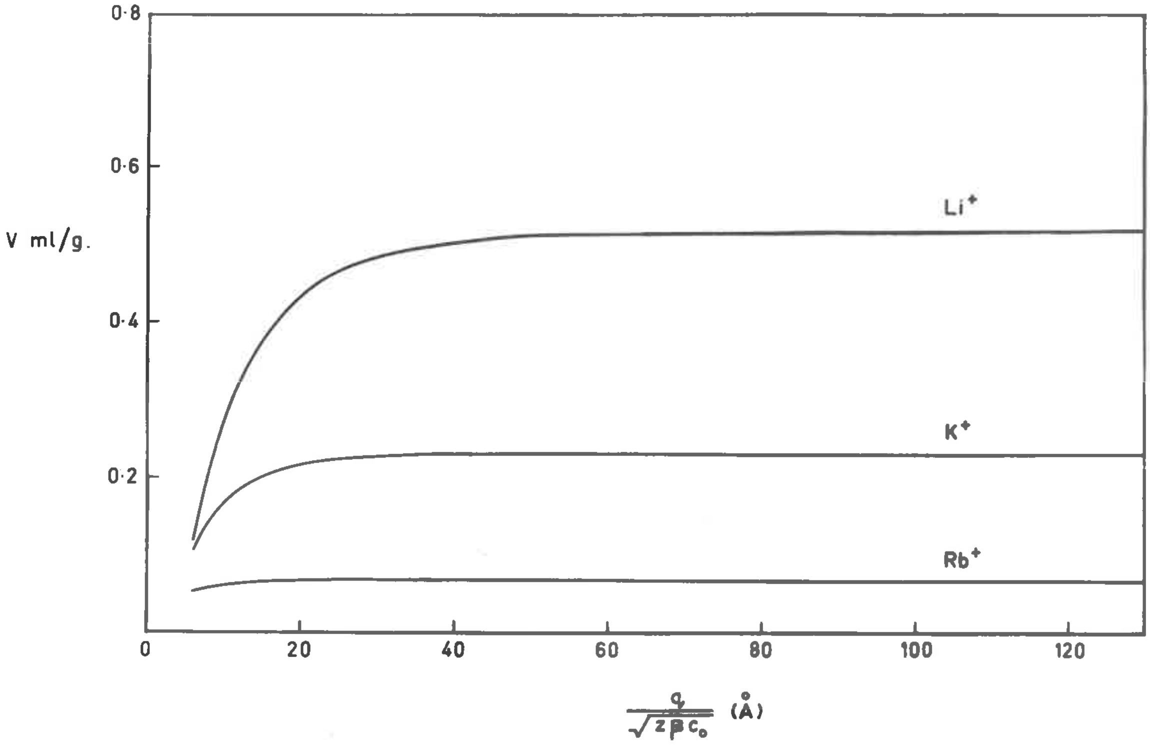


FIGURE 11.

The difference in charge between the permanent negative charge carried by the clay surface and the bound charge is equal to the nett negative charge in the diffuse layer. Assuming that the nett diffuse layer charge is effectively constant over the experimental concentration range, and uniformly distributed at the Stern-diffuse layer boundary, expected chloride exclusion volumes for a series of charge densities (Table 9) can be calculated. Expected exclusion volumes from a surface area of 110 m^2/g. for charge densities of 15, 10, 0.4 and 0.1 x 10^4 e.s.u./cm^2 are plotted in Fig. 12. Apart from the Cs illite, where the charge density is zero, all the other derived charge densities (Table 9) would be expected to give curves that are essentially linear, possessing a slope equivalent to the maximum available area of 110 m^2/g. Little or no reduction in derived area is to be expected until the charge density falls below about 0.4 x 10^4 e.s.u./cm^2 when the curves, particularly at the higher electrolyte concentrations are no longer linear. However, the experimental curves (Fig. 9) show considerable reductions in surface area without becoming curvilinear.

The decrease in diffuse layer charge was considered in terms of the mass action law between the cations and the surface, assuming that the exchange sites are identical and completely independent. The ion-site interaction can be represented as

$$\text{free site} + \text{ion} \rightleftharpoons \text{combined site}$$

Let the equilibrium condition at any such site be designated by its degree of association α, which is the probability of an ion being bound

THEORETICAL EXCLUSION VOLUMES FROM THE DIFFUSE LAYER AT DIFFERENT CHARGE DENSITIES (BASED ON AN AREA OF 110 m^2/g.)

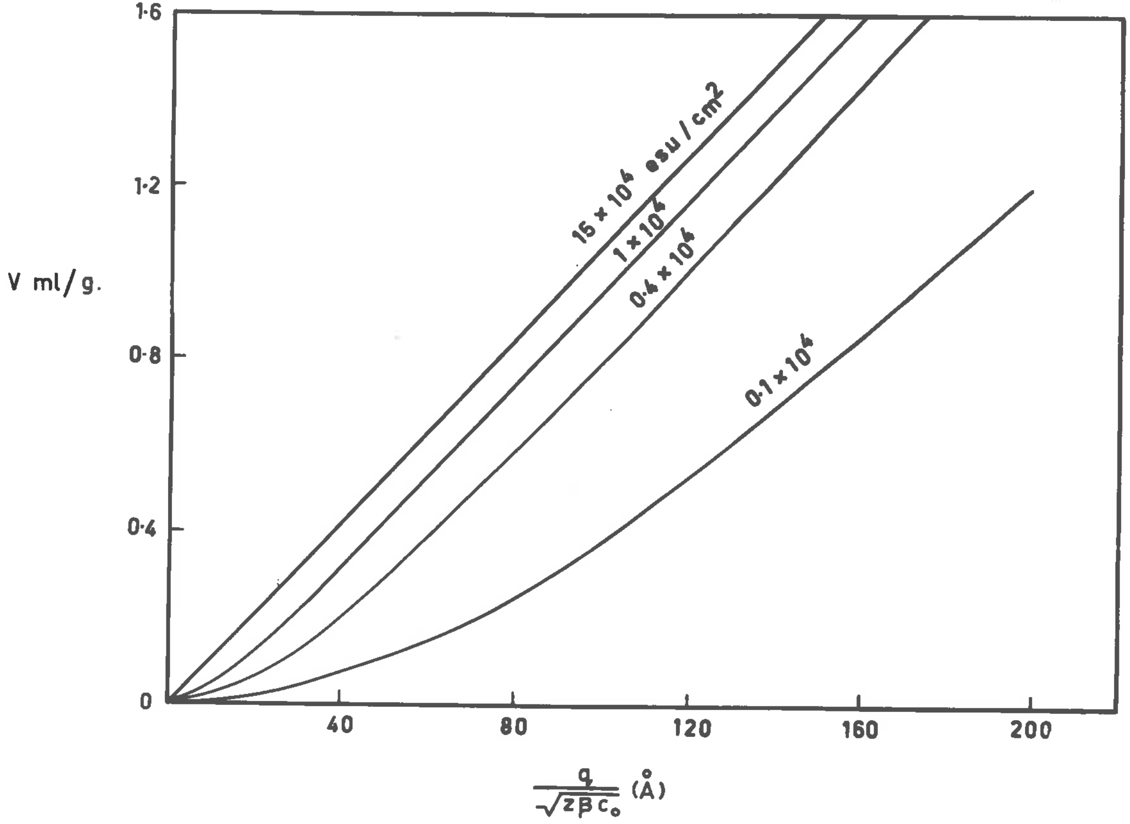


FIGURE 12.

TABLE 9

POSTULATED REDUCED DIFFUSE LAYER CHARGE DENSITIES OF HOMO-IONIC FITHIAN ILLITES (ASSUMING REDUCTION IN CHARGE PROPORTIONAL TO REDUCTION IN AREA).

Exchangeable cation	Fraction of ions bound	Diffuse layer charge density e.s.u./cm^2
-	0	-8.17×10^4
Li^+	0.273	-5.94×10^4
Na^+	0.364	-5.20×10^4
K^+	0.677	-2.64×10^4
Rb^+	0.905	-0.78×10^4
Cs^+	1.000	0

at a particular site; in other words, α represents the fraction of such sites at which an ion is bound. The equilibrium condition then becomes:-

$$\frac{\alpha}{1-\alpha} = kC \tag{68}$$

where $1 - \alpha$ is the uncombined fraction

k is the association constant for the reaction

C is the molar electrolyte concentration

Equation (68) was applied to the chloride exclusion data for potassium Fithian illite. An association constant (k = 698.7) was calculated on the assumption that 67.7% of the sites were combined at .003 N electrolyte concentration. This figure is based on the assumption that the reduction in charge is proportional to the reduction in area (Table 9). The association constant was then applied to a series of other concentrations and diffuse double layer theory was used to calculate the potentials operative at the various effective diffuse layer charge densities. Depth of chloride exclusion were then calculated using Overbeek's anion exclusion theory (equation (42), this thesis). These data are presented in Table 10.

The total surface area of 110 m^2/g. was then used to calculate the expected volumes of chloride exclusion, which are plotted in Fig. 13. The two most significant features of this curve are the slope of 125 m^2/g. and the intercept of about 20 Å on the abscissa, which indicates that there is virtually zero exclusion at electrolyte concentrations greater than about 0.1 molar. Comparison of this plot with the

Mass action analysis of K^+ Fithian illite results.

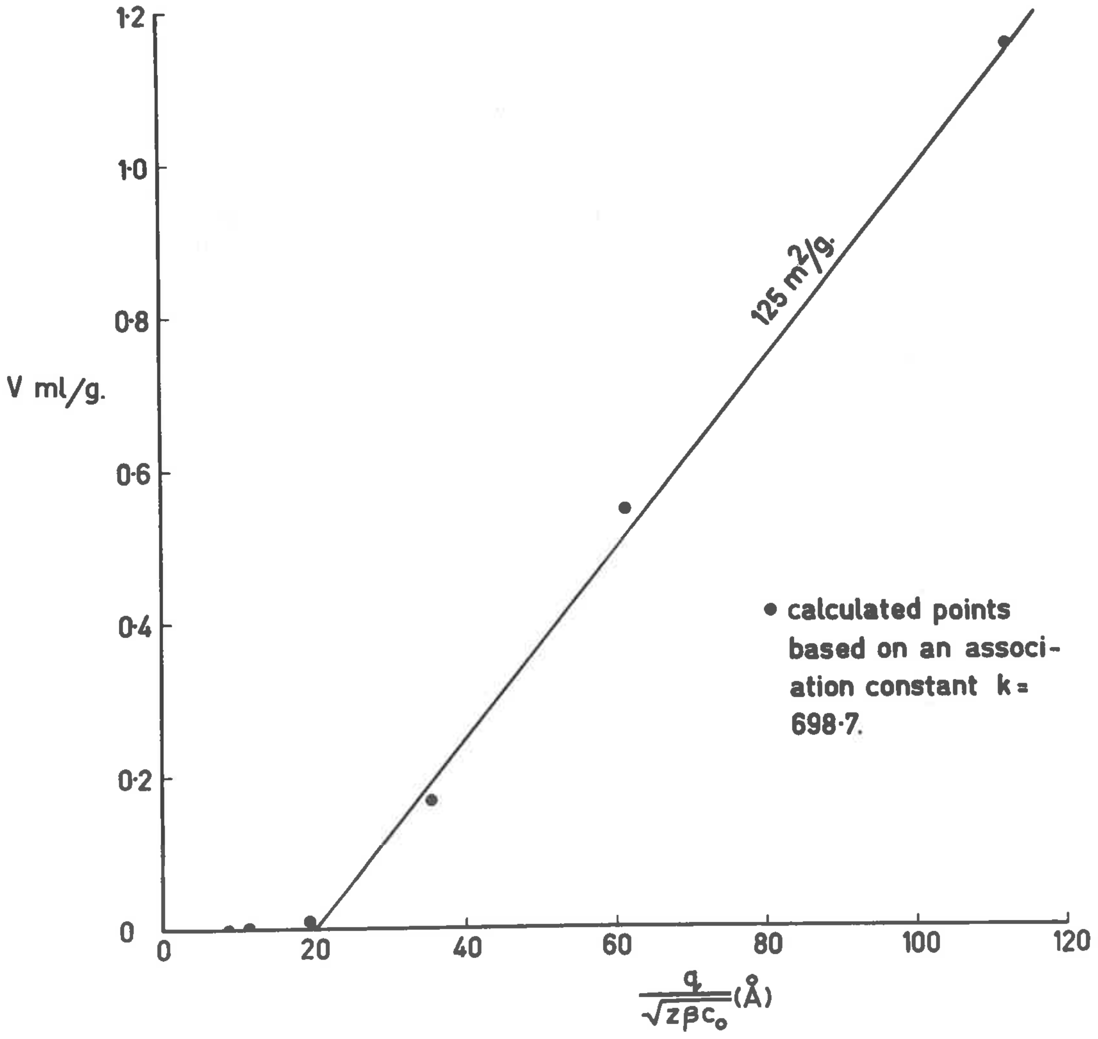


FIGURE 13.

TABLE 10

CHLORIDE EXCLUSION FOR POTASSIUM FITHIAN ILLITE

ASSUMING ION-SURFACE ASSOCIATION IS A FUNCTION OF CONCENTRATION

$k = 698.7$ (.003N)

Concn.	α	σ_d Effective diffuse layer charge density esu/cm^2	meq./cm^2	ψ_o mV.	α_-	Γ_- meq./cm^2	$\frac{\Gamma_-}{C_o}$ Å
0.003	0.677	2.639×10^{4}	0.903×10^{-7}	-167.6	0.0350	0.0316×10^{-7}	105.3
0.01	0.874	1.029×10^{4}	0.352×10^{-7}	-90.91	0.1420	0.0500×10^{-7}	50.0
0.03	0.954	0.376×10^{4}	0.129×10^{-7}	-29.59	0.3577	0.0461×10^{-7}	15.37
0.1	0.986	0.114×10^{4}	0.0391×10^{-7}	-6.71	0.4668	0.0183×10^{-7}	1.83
0.3	0.995	0.0409×10^{4}	0.0140×10^{-7}	-1.45	0.4924	0.00689×10^{-7}	0.23
0.5	0.997	0.0245×10^{4}	0.0084×10^{-7}	-0.50	0.4969	0.00417×10^{-7}	0.08

experimental data for K^+ Fithian illite presented in Fig. 9, leads to the conclusion that a simple ion association-dissociation equilibrium coupled together with a homogeneous charge distribution at the Stern-diffuse layer boundary does not provide an adequate explanation of the data.

2. Ion Association.

It was somewhat surprising that a straight line relationship was obtained when the results were plotted according to Schofield's equation (39), since double layer theory predicts that lowered charge densities would lead to curvilinear plots. The inability of the diffuse double layer analysis to explain the results is ascribed to ion binding on discrete areas of surface, occasioned by the relative immobility of the bound ion. Consequently, the charge at the Stern-diffuse layer boundary can no longer be treated as an average charge uniformly smeared over this boundary.

The fact that all the measured areas are considerably less than the expected 110 m^2/g. suggests that the full stoichiometric charge density is not operative for any cation, while the linear form of Schofield's plot indicates that the measured charged surface areas must be constant, with exclusion occurring from discrete charged sites. These sites are considered to be associated with a unit charge giving rise to an exclusion volume of side $2/K$, which represented the volume of the ionic atmosphere associated with a singly charged ion. For a 1:1 electrolyte $2/K$ is the first term in equation (39).

The area of exclusion would thus be given by

$$A = N\left(\frac{2}{K}\right)^2 = N\,\frac{B}{C_o} \quad \ldots\ldots\ldots \quad (69)$$

where B is a constant. N is the number of sites at which the cations have sufficient mobility to allow them to take part in double layer formation. These cations then become indistinguishable from electrolyte cations. N is thus not the degree of dissociation in the accepted sense (see p.77), but simply represents the number of ions possessing normal mobility as discussed by Overbeek (1956). Further, since A is found to be constant, N must be proportional to C_o. Such a relationship may be derived from a consideration of the structure of the diffuse layer outlined earlier.

The work of Verwey and Kruyt (1933) and DeBruyn (1942) on the silver iodide sol has shown that the diffuse double layer has its origin in the equilibrium distribution of potential determining silver or iodide ions between the particle surface and the sol medium. The double layer in these systems is formed by the adsorption of these potential determining ions from solution, whereas on clay mineral surfaces the double layer is formed through the dissociation of exchangeable ions from the surface. In each case, the resulting double layer potential is given by

$$\psi_o = \frac{RT}{F}\ln\frac{C_o}{C_I} \quad (70)$$

where C_o is the bulk electrolyte concentration and C_I is the concentration of potential determining (or exchangeable) ions when all the exchangeable ions have sufficient mobility to engage in diffuse layer formation. C_I will vary with the cationic species, and also be independent of bulk electrolyte concentration.

The diffuse layer charge density σ_d, the bulk electrolyte concentration C_o and the diffuse layer potential ψ_o are related according to equation (10) viz.

$$\sigma_d = \sqrt{\frac{C_o \varepsilon kT}{2\pi}} \left\{ \exp\left(\frac{ze\psi_o}{2kT}\right) - \exp\left(-\frac{ze\psi_o}{2kT}\right) \right\} \tag{71}$$

Substituting for ψ_o in equation (71) and re-arranging after eliminating $\exp\left(-\frac{ze\psi_o}{2kT}\right)$ which is assumed to be vanishingly small,

$$\sigma_d = \sqrt{\frac{\varepsilon kT}{2\pi}} \cdot \sqrt{C_o} \cdot \frac{\exp}{2}\left(\ln \frac{C_o}{C_I}\right) \tag{72}$$

i.e. $$\sigma_d = B' \frac{C_o}{\sqrt{C_I}}$$

where B' is a constant $= \sqrt{\frac{\varepsilon kT}{2\pi}}$

Now the diffuse layer charge density must also be given by the number of exchangeable ions that are in the diffuse part of the double layer per unit area of surface:-

$$\sigma_d = \frac{N}{A_o} \tag{73}$$

Combining equations (72) and (73) gives

$$N = B'A_o \frac{C_o}{\sqrt{C_I}}$$

$$\text{or } N = A_o K' C_o \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (74)$$

where K' is equal to $B'/\sqrt{C_I}$.

Thus, the number of exchangeable ions possessing normal mobility and present in the diffuse part of the double layer may be seen to be a linear function of the bulk electrolyte concentration. As the concentration increases, the diffuse layer potential ψ_o decreases and the electrostatic forces tending to immobilize ions in the adsorbed layer decrease. The nett result is thus a release of exchangeable ions into the diffuse layer.

The area A is seen to be the geometric area covered by the ionic atmospheres of the mobile exchangeable ions that are present in the diffuse layer. Since this area is found to be constant for a given homo-ionic system, as the electrolyte concentration is decreased and the size of the diffuse layer ion atmospheres increases, there is a complete compensation between charged area and the number of diffuse ion atmospheres.

The volume of exclusion from the ionic atmospheres of the mobile counter-ions may be written as

$$V = N\left(\frac{2}{K}\right)^3 = C_o \frac{B'}{C_o^{3/2}} = \frac{B'}{\sqrt{C_o}} \quad \ldots\ldots\ldots\ldots \quad (75)$$

This expression may be formally identified with Schofield's negative adsorption equation in which the depth (volume) of exclusion is inversely proportional to the square root of the electrolyte concentration.

Since the experimentally measured surface areas A are always less than the maximum available area A_o, the actual number of associated ions, will always be greater than the number N_o required to give the maximum area.

The number of mobile cations necessary to give the particular experimental areas may be calculated for any arbitrary electrolyte concentration C_o, e.g. 0.1 molar, where the area associated with each ion is 372 $Å^2$ (i.e. $\left(\frac{2}{K}\right)^2$). The number of ions required to completely cover an area A_o of $110 m^2/g$. is then approx. 3×10^{19}. Now, the stoichiometric charge density of 2.80×10^{-7} meq./cm^2 gives an area associated with each charged site of about 59 $Å^2$. Thus, the diffuse layer charge density required to give complete exclusion from the full area A_o at an electrolyte concentration of 0.1 molar is $\frac{59}{372}$ = 16% of the stoichiometric charge density. Thus, at this concentration there is a basic binding fraction of 84%. A further binding fraction dependent on the particular homo-ionic system has to be included. The total binding fractions for electrolyte concentrations of 0.1 and 0.01 molar are shown in Table 11.

The relative degrees of ion association that have been postulated in this thesis are very similar to those of Mattson (1929) and Davis (1942) for ion association at bentonite surfaces. Associated ions are considered to exist either as Fuoss ion pairs with the counter-

TABLE 11

FITHIAN ILLITE

Cation	Fractional Area Measured A/A_o	Binding Fractions	
		0.1 Molar	0.01 Molar
Li	0.727	84 + 16 x .273 = 88.4	98.4 + 1.6 x .273 = 98.8
Na	0.636	84 + 16 x .364 = 89.8	98.4 + 1.6 x .364 = 99.0
K	0.323	84 + 16 x .667 = 94.7	98.4 + 1.6 x .667 = 99.5
Rb	0.095	84 + 16 x .905 = 98.5	98.4 + 1.6 x .905 = 99.9
Cs	0	84 + 16 x 1.0 = 100	98.4 + 1.6 x 1.0 = 100

ion bound in the I.H.P. or as Bjerrum ion pairs with binding occurring in the O.H.P. one or possibly two (Posner and Quirk, 1964) water layers removed from the clay mineral surface. It is the un-paired charges, which are electrically balanced by the mobile diffuse layer cations that are the determinants of chloride exclusion, i.e. the charged area is a most important parameter in determining the exclusion of chloride. In fact, the measured area provides an estimate of the free energy of formation of diffuse double layers per unit weight of clay. Conversely, the differences between the total area and observed area are measures of the binding energy per unit weight of clay.

3. Development of General Binding Theory.

The free energy of a double layer system involving a negatively charged surface may be defined as the total energy required to move all the repelled anions up to that surface. The general expression for the free energy of formation of a double layer per unit area of surface is

$$G = -\int_{0}^{\Psi_0} \sigma d\Psi \tag{76}$$

where G = free energy of double layer formation per cm^2 surface

σ = surface charge density

Ψ_0 = surface potential

Overbeek (in Colloid Science, editor Kruyt, 1952) derived the following expression for the free energy of a large flat diffuse double layer, after substituting for the charge density σ in terms of potential and concentration, viz.

$$G = -\sqrt{\frac{2\varepsilon nkT}{\pi}} \int_0^{\psi_0} \sinh \frac{ze\psi}{2kT}\, d\psi$$

$$= -\frac{8nkT}{K}\left(\cosh \frac{ze\psi_0}{2kT} - 1\right) \qquad (77)$$

where n is the number of ions/ml in a solution of concentration C_o.

To equate the various forces that are acting it is necessary to define a reference concentration:- this was chosen as the concentration at which the area of the ionic atmosphere (i.e. $(^2/K)^2$) is equal to the charge density of the clay surface, or more particularly the area of surface associated with each charged site. For Fithian illite, the charge density $\sigma = 8.17 \times 10^4$ e.s.u./cm^2 corresponds to one charge per 59.4 Å^2 of surface. The corresponding reference electrolyte concentration is then 0.628 N. If no ion binding occurred, i.e. all the exchangeable ions were dissociated, the full surface area A_o = 110 m^2/g. would have been measured by chloride exclusion. In this case the total free energy of diffuse double layer formation, with the full stoichiometric charge density σ and the maximum available area A_o operative is

$$G_o = -\frac{8A_onkT}{K}\left(\cosh \frac{ze\psi_o}{2kT} - 1\right) \qquad (78)$$

G_o is thus the maximum possible free energy of diffuse layer formation per unit weight of clay.

Because the charges on a clay surface arise from isomorphous replacement in the crystal lattice, they can be regarded as fixed or discrete. When ion binding occurs at particular discrete sites, either Fuoss or Bjerrum type ion pairs are formed, depending on the ion. These ion pairs have no electrostatic effect on any free ions in the system. Further, when related to the reference state, the charge and potential of the dissociated, (but also discrete) sites remains unaltered. Thus, even in the limit of very few charged sites on the clay mineral surface, equation (78) would still hold for the charged areas at the reference concentration. Thus at this concentration, the free energy of diffuse double layer formation on the charged areas A ($A < A_o$) is given by

$$G_s = -\frac{8AnkT}{K}\left(\cosh\frac{ze\Psi_o}{2kT} - 1\right) \qquad (79)$$

The area A is the measured area obtained from the chloride exclusion plots, and represents that area due to the development of ionic atmospheres about the charged sites the number of which has been shown (p. 82) to be concentration dependent. In the range of electrolyte concentrations used in this work, the area of exclusion for each dissociated (free) cation will be much greater than the area of 59.4 $Å^2$ calculated for the reference concentration. It should be emphasized that it would be extremely difficult to calculate the charge and potential distributions at the lower concentrations when the individual ionic atmospheres spread out over much larger areas of surface. At the reference concentration the distribution is completely discrete, and equal to σ_δ. (Fig. 14).

The reduction in diffuse double layer development or alternatively the energy of association of a particular ion with the clay mineral surface is given by

$$\mathcal{G}_o - \mathcal{G}_s = -\frac{8(A_o - A)nkT}{K}\left(\cosh\frac{ze\psi_o}{2kT} - 1\right) \tag{80}$$

At the reference concentration, the potential on free sites when a large amount of binding has occurred is exactly the same as that on the free areas when little or no ion binding has occurred. Any comparisons between the different exchangeable cations will have to be made at the same electrolyte concentration. The reference concentration will be used to make these comparisons. This, however, is not a particularly rigorous condition, because it may be seen from Table 12, that the parameter $\frac{n}{K}\left(\cosh\frac{ze\psi_o}{2kT} - 1\right)$ is fairly insensitive to changes in electrolyte concentration. Thus the free energy of diffuse double layer formation for surfaces of charge density 8.17×10^4 e.s.u./cm^2 will not be particularly dependent on electrolyte concentrations varying from 0.003 - 0.3 molar.

The energy of association of an ion with the surface per unit weight of clay is thus related to the reduction in area due to the binding of exchangeable cations on particular discrete areas of surface.

Ion dissociation from discrete charged sites.

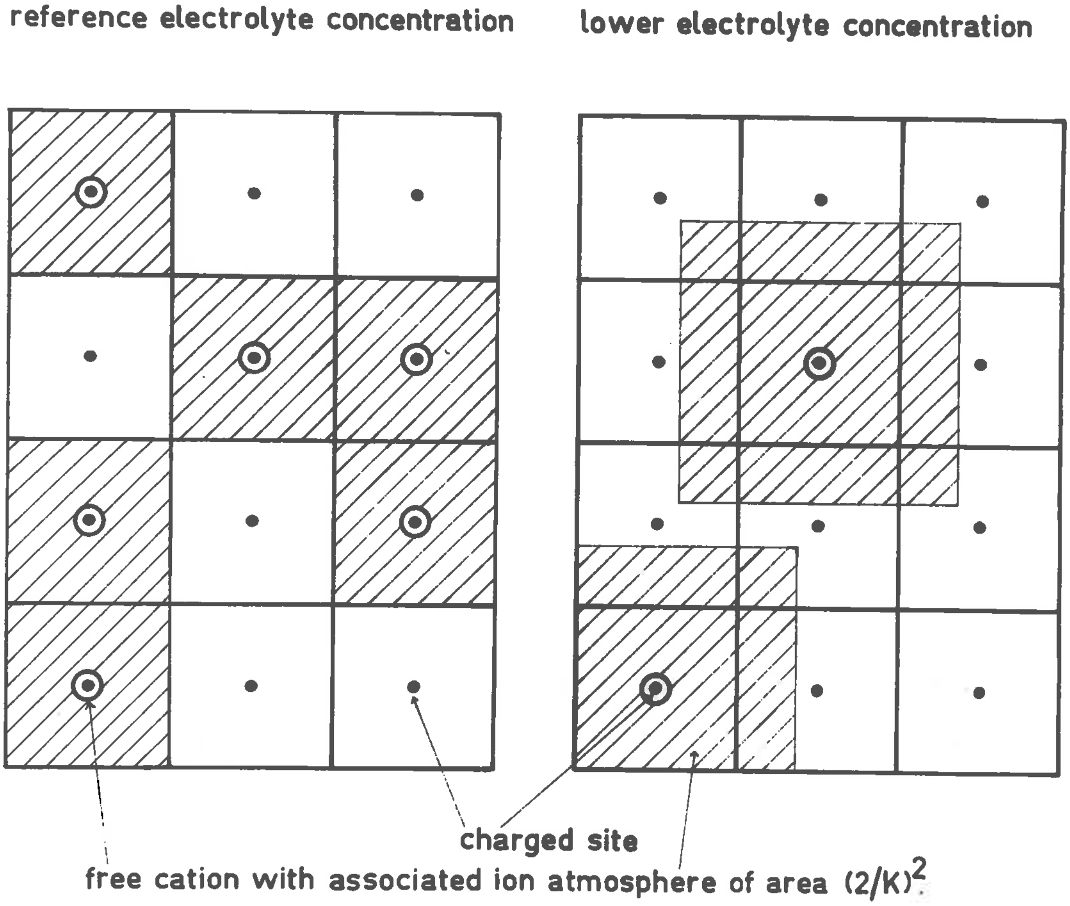


FIGURE 14.

TABLE 12

Values for Parameter $\frac{n}{K}\left(\cosh\frac{ze\psi_o}{2kT}-1\right)$ for Fithian Illite

in a 1:1 electrolyte $\sigma = 8.17 \times 10^4$ esu/cm^2

Electrolyte concn.	1/K	$\frac{n}{K}\left(\cosh\frac{ze\psi_o}{2kT}-1\right)$
meq./ml.	Å	
0.628 (REF.)	3.85	30.00×10^{12}
0.3	5.61	34.16×10^{12}
0.1	9.66	37.23×10^{12}
0.03	17.77	40.14×10^{12}
0.01	30.54	40.92×10^{12}
0.003	56.1	42.17×10^{12}

Furthermore, the energy of association would be expected to be related to the nett electrostatic energy between a cation and the charged surface. A term to account for the energy of partial desolvation may also be required. The magnitude of this term will depend on whether the ion is bound "Fuoss-like" in the inner Helmholtz plane or whether it is bound in the outer Helmholtz plane as part of a Bjerrum ion pair. An ion bound in the I.H.P. is considered to be at least partially desolvated, with no water molecules existing between it and the charged surface. Since the alkali metal cations exist and move in solution as hydrated entities, the partial desolvation requirement for binding may simply involve a partial displacement of the hydration sheath. However, as the ion moves into the I.H.P. there will also be a concurrent re-arrangement of the water molecules in the primary water layer. Posner and Quirk (1964) showed that there were three surface regions on montmorillonite and illite into which electrolyte could penetrate under particular bulk electrolyte concentrations. The first region, which is never penetrated by electrolyte corresponded to the primary hydration shell of the cation. They considered that entry "into the other regions is governed by the image force between the ions and the surface region, and hence the difference between the dielectric constant of the bulk and surface water. When these approach equality entry is controlled by the need for electrolyte ions to undergo suitable ion pairing and to decrease the entropy of an already ordered surface, rendering it more like the electrolyte solution. The ability of an electrolyte to enter the surface regions is correlated with the balance between the relative structure making and breaking power of an ion. The free energy of penetration of an electrolyte into the adsorbed water increases with decreasing hydration." Thus the large, relatively unhydrated caesium ion will show an increasing tendency to be bound at the I.H.P. Furthermore, for any given ion, a much smaller partial desolvation requirement would be needed if an ion is bound in the O.H.P.

It was shown earlier (equation (64)) that the nett electrostatic energy between a cation and a negatively charged surface depends on the difference in dielectric constant between the adsorbed region and the diffuse layer. Assuming a dielectric constant of 6 for the primary adsorbed water layer (see p. 48) and a macroscopic dielectric constant of 80 for the diffuse layer, the nett electrostatic energy tending to accumulate ions into the adsorbed layer was calculated. The attractive energy between the cation and the surface, the image force repulsion energy and the resultant nett energy have been plotted in Fig. 15, for a monovalent cation approaching a planar surface of charge density 8.17×10^4 e.s.u./cm^2. The resultant curve shows a very large initial repulsive force, which decreases very rapidly with distance from the surface, until a distance of 2.1 Å is reached, at which distance the nett force has dropped to zero. Thereafter a more gradually changing nett attractive force is obtained.

London-van der Waal's attractive forces between an ion and the crystal surface, calculated on the assumption that there are seven

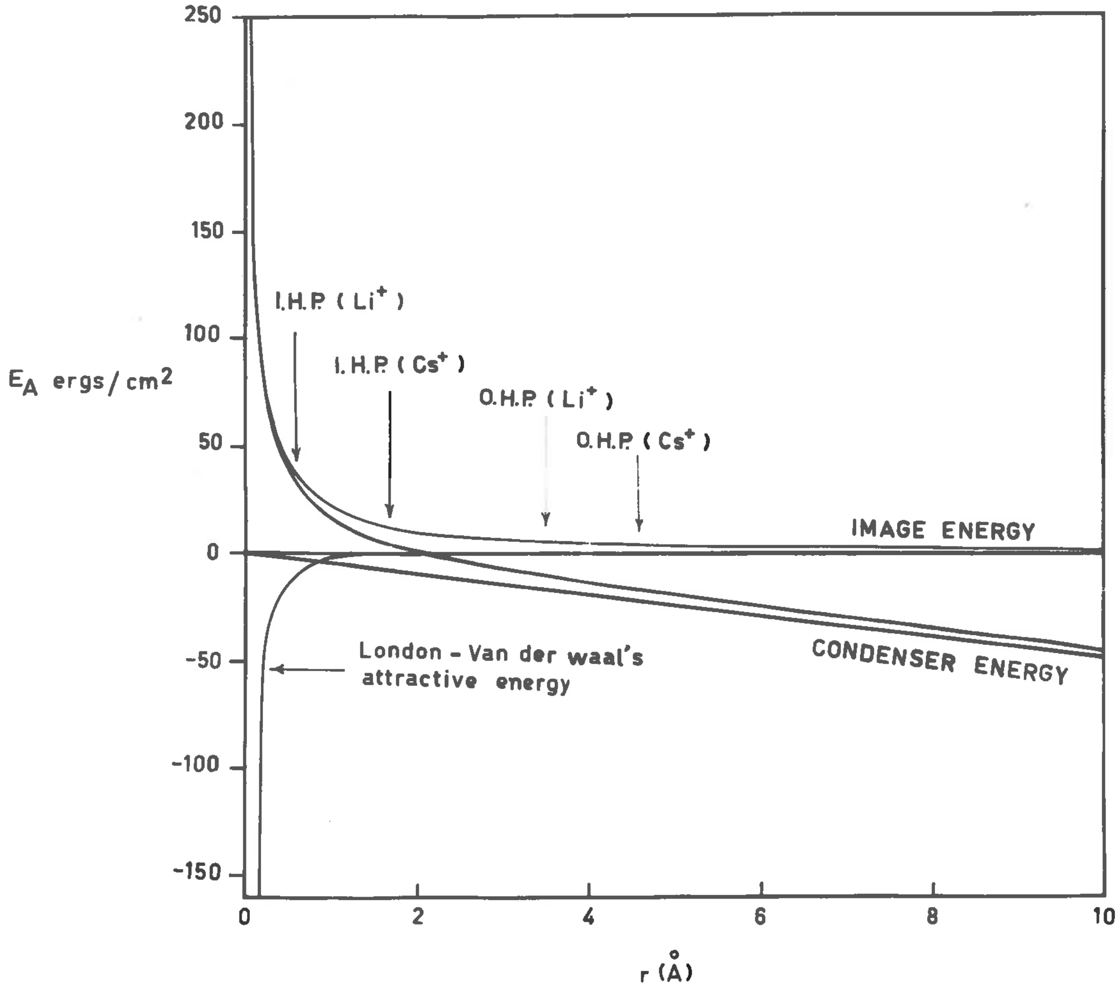

ENERGY OF INTERACTION BETWEEN MONOVALENT CATIONS AND AN ILLITE SURFACE OF CHARGE DENSITY $8{\cdot}17 \times 10^4$ esu/cm^2

FIGURE 15.

sheets per illite crystal are also plotted in Fig. 15. These forces may be omitted from further consideration, since they are relatively insignificant until the ion approaches to within 0.5 Å of the surface.

When an ion is present in the adsorbed region its distance of closest approach to the surface will be equal to the ionic radius. Thus, a Li^+ ion can approach to within 0.60 Å of the surface, while a Cs^+ ion cannot approach any closer than 1.69 Å. A Li^+ ion distant 0.60Å from the surface will experience a far greater repulsive force tending to expel it into the diffuse layer than a Cs^+ ion situated 1.69 Å from the surface. Thus, there is a greater tendency for Cs^+ ions than Li^+ ions to accumulate in the I.H.P. situated at a distance equal to the ionic radius from the surface. In accord with these considerations, the experimental results show that the amount of ion binding is greater the larger the ionic radius.

The next well defined position near to the surface at which a cation may reside will be the O.H.P., where the cation may also be bound by electrostatic forces but less strongly than in the I.H.P. This is separated from the I.H.P. by a single water layer and may be identified with the boundary between the adsorbed and diffuse parts of the double layer. It may be seen from Fig. 15 that a Li^+ ion at the O.H.P. experiences a smaller attractive force tending to pull it into the I.H.P. than a Cs^+ ion. The nett result of the balance of forces between the I.H.P. and O.H.P. is that the binding of exchangeable cations in the I.H.P. increases with increasing ion size in the alkali group of metals.

The O.H.P. will also represent the distance of closest approach of the repelled anions to the surface.

Binding of an ion at the charged surface will be governed by the balance of forces at the I.H.P. together with a nett electrostatic energy term which must accompany binding. The free energy of complete desolvation per ion, by analogy with the Born hydration energy is given by

$$\Delta G_I = - \frac{z^2 e^2}{r} \cdot \frac{(\varepsilon_m - \varepsilon_w)}{\varepsilon_w \cdot \varepsilon_m} \tag{81}$$

The free energy of desolvation per cm^2 surface is thus

$$\Delta G_s = - \frac{ze\sigma}{r} \cdot \frac{(\varepsilon_m - \varepsilon_w)}{\varepsilon_w \cdot \varepsilon_m} \tag{82}$$

where ϵ_m = dielectric constant of the primary water layer

ϵ_w = macroscopic dielectric constant of water

r = ionic radius

The dielectric constant differences in equations (81) and (82) are negative, because the water expelled from the ion during desolvation will be transferred from a region of lower to a region of higher dielectric constant.

The combined electrostatic energy of attraction and partial desolvation energy terms may now be equated to the reduction in total free energy due to ion binding, given by equation (80). Expressing all energy terms in units of $ergs/cm^2$ of surface, the following relationship is obtained:-

$$\frac{(\varepsilon_w-\varepsilon_m)\sigma ze}{\varepsilon_w(\varepsilon_w+\varepsilon_m)2r}-\frac{2\pi\sigma^2 r}{(\varepsilon_w+\varepsilon_m)}-\frac{z\sigma e(\varepsilon_m-\varepsilon_w)}{r.\,\varepsilon_w.\,\varepsilon_m}=-\frac{8nkT}{K}\left(\cosh\frac{ze\psi_0}{2kT}-1\right) \tag{83}$$

Multiplying by the area per g. of clay allows the energy terms to be expressed as ergs/g. clay

$$\frac{A_0(\varepsilon_w-\varepsilon_m)\sigma ze}{\varepsilon_w(\varepsilon_w+\varepsilon_m)2r}-\frac{2A_0\pi\sigma^2 r}{(\varepsilon_w+\varepsilon_m)}-\frac{A_0\sigma ze(\varepsilon_m-\varepsilon_w)}{r.\,\varepsilon_w.\,\varepsilon_m}=-\frac{8(A_0-A)nkT}{K}\left(\cosh\frac{ze\psi_0}{2kT}-1\right) \tag{84}$$

The area term on the right is $(A_o - A)$ because the binding energy is being equated, and not the free energy of double layer formation. Hence

$$\frac{A_0-A}{A_0}=\frac{-(\varepsilon_w-\varepsilon_m)K\sigma ze}{r.\varepsilon_w(\varepsilon_w+\varepsilon_m)16nkT\left(\cosh\frac{ze\psi_0}{2kT}-1\right)}+\frac{\pi\sigma^2 Kr}{(\varepsilon_w+\varepsilon_m)4nkT\left(\cosh\frac{ze\psi_0}{2kT}-1\right)}$$

$$+\frac{ze\sigma(\varepsilon_m-\varepsilon_w)Kp}{r.\varepsilon_w.\varepsilon_m.8nkT\left(\cosh\frac{ze\psi_0}{2kT}-1\right)} \tag{85}$$

where p is a factor < 1, taking partial desolvation into account. Multiplying both sides of equation (85) by r gives

$$r\theta=\frac{-(\varepsilon_w-\varepsilon_m)K\sigma ze}{\varepsilon_w(\varepsilon_w+\varepsilon_m)16nkT\left(\cosh\frac{ze\psi_0}{2kT}-1\right)}+\frac{ze\sigma(\varepsilon_m-\varepsilon_w)Kp}{\varepsilon_w.\varepsilon_m.8nkT\left(\cosh\frac{ze\psi_0}{2kT}-1\right)}$$

$$+\frac{\pi\sigma^2 Kr^2}{(\varepsilon_w+\varepsilon_m)4nkT\left(\cosh\frac{ze\psi_0}{2kT}-1\right)} \tag{86}$$

where $\theta = \frac{A_o - A}{A_o}$ is the ratio of the areas and also the number of sites, at the reference concentration, at which binding has occurred, to the total number of sites.

4. Application of Binding Theory to Experimental Results

The chloride exclusion data for the monovalent Fithian illite systems were plotted in Fig. 16, according to equation (86) using the hydrated ionic radius r. The use of the hydrated radius has been preferred to that of the ionic radius, because as suggested by Frank and Evans (1945), there is a rather firmly oriented layer of water molecules in the immediate vicinity of the ion. Latimer (1936) considered that the effective radius was that of the bare ion together with 2.8 Å for the first rigidly held layer of water molecules. Immediately outside this rigidly held layer, the medium is treated in terms of the ordinary macroscopic dielectric constant. This picture is quite consistent with the more modern treatments (Ritson and Hasted, 1948) of water structure around ions, which show that the first layer of adsorbed water molecules is a region of appreciable dielectric saturation. This suggests that the ions should be treated as possessing a primary hydration sheath. Furthermore, when such a solvated ion moves up to the adsorbed region of the double layer it is considered to have moved from a region of high dielectric constant ($\epsilon_w = 80$) to a region of low dielectric constant ($\epsilon_m = 6$). It is considered that the use of the dielectric constant of the adsorbed layer, rather than that of the clay mineral ($\epsilon_m = 2$) is essentially more correct, because the bound ions, although held directly at the charged sites, are still present in the primary water layer associated with the surface, and are not an integral part of the charged surface itself. Thus, counter to the views

BINDING OF ALKALI METAL CATIONS ON FITHIAN ILLITE SURFACES

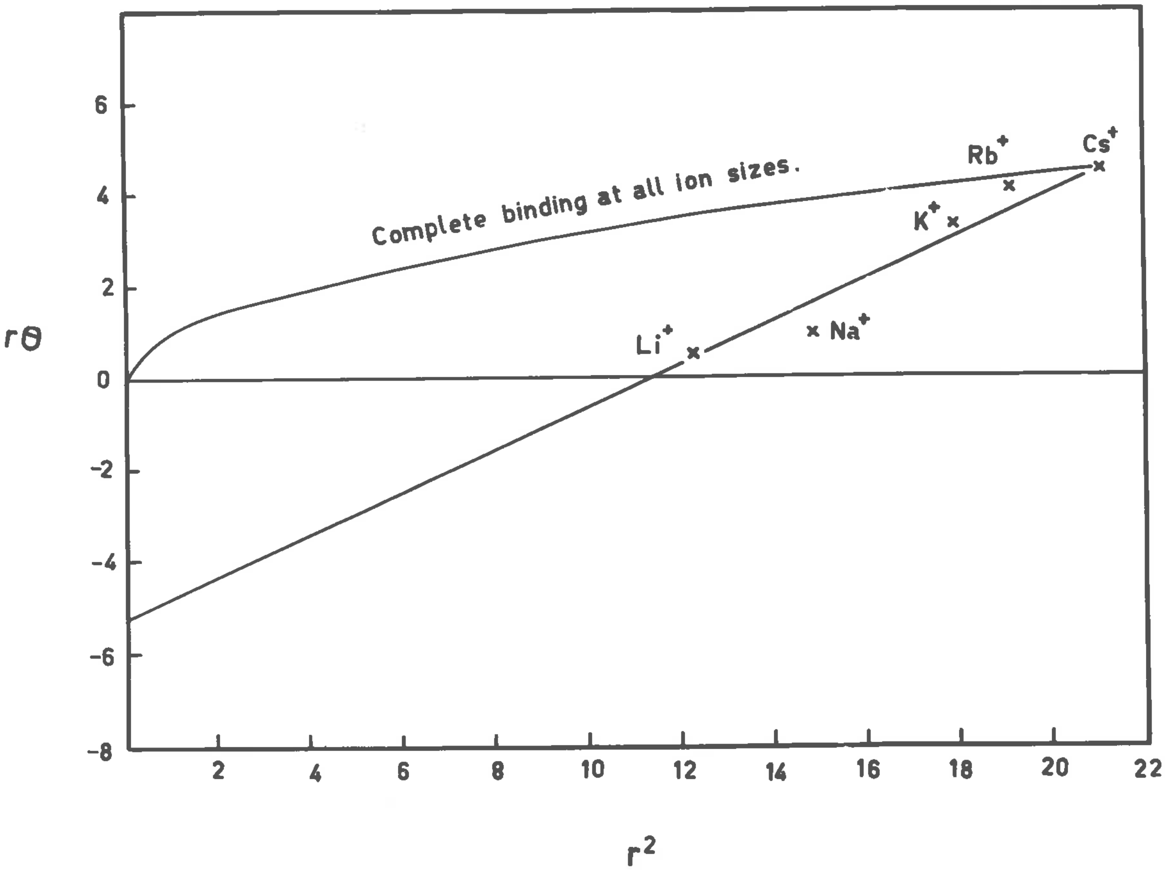


FIGURE 16.

of Jordine, Bodman and Gold (1962) ion adsorption at clay mineral surfaces is considered to be independent of the dielectric constant of the clay mineral itself. These ideas agree with those of Posner and Quirk (1964) who considered that an ion interacting with a surface moves from the bulk solution into a layer of surface adsorbed water of very much lower dielectric constant.

The equation of the straight line obtained from the plot in Fig. 16, is

$$r\theta = -5.18 + 0.46r^2 \tag{87}$$

where the intercept and slope may be identified with corresponding terms in equation (86). This equation was solved theoretically for the reference electrolyte concentration of 0.628 N. Neglecting the intercept term arising because of partial ion desolvation, the relationship obtained is

$$r\theta = -2.17 + 0.51r^2 \tag{88}$$

The agreement between the experimental and theoretical values of slope is remarkably good, particularly in view of the somewhat limited knowledge of the structure and properties of water both at interfaces and in the immediate vicinity of ions. The lack of agreement between the intercepts however, suggests that re-orientation of water molecules prior to ion binding may play an important part in the energy relationships of the adsorbed ions. The intercept obtained from the desolvation term based on the Born hydration energy concept is given by (from equation (86)):-

$$\frac{\sigma z e\,(\varepsilon_m - \varepsilon_w)\,Kp}{\varepsilon_m \cdot \varepsilon_w \cdot 8nkT\left(\cosh \frac{ze\psi_0}{2kT} - 1\right)}$$

If total desolvation occurred during or as a prerequisite to ion binding (p = 1) the expected contribution of this term to the intercept would be - 62.3 Å. However, as discussed above, a far more realistic physical model is one in which the cations are only partially desolvated prior to binding. Alternatively, energy may be lost through re-orientation of the water molecules in the primary water layer, allowing the cation to come into contact with the charged surface and be bound as a Fuoss ion pair. In fact, both mechanisms for the re-arrangement of water molecules will be occurring simultaneously. If the energy loss due to the change in the water structures is only about 5 per cent of the total given above (i.e. p = 0.05) the intercept term becomes - 3.11 Å. On adding this to the image force intercept, the theoretical equation now becomes

$$r\theta = -5{\cdot}28 + 0{\cdot}51r^2 \qquad (89)$$

The observed and theoretical intercepts are now of the same magnitude. The apparent agreement between the observed and theoretical equations suggests that ion binding is purely electrostatic in origin, and that specific ion - site interactions are not important in the general phenomenon of ion binding on the Fithian illite external crystal surfaces.

The amount of desolvation necessary before an ion is bound increases with decreasing ion size, and thus, increasing ion hydration. Accordingly the results were plotted in Fig. 17, in a form similar to the "specific adsorbability" function of Bockris, Devanathan and Muller (1963), for the adsorption of ions on a metal surface. In this model, which is purely electrostatic in origin, θ from the derived general equation (86) of ion binding is plotted as a function of the ionic radius. Fig. 17 shows that the relatively unhydrated ions are bound to a greater extent as a result of the balance of forces near the surface, together with the fact that less energy is required for partial desolvation before binding. Bockris (1949) obtained the primary hydration numbers of the alkali metal ions by averaging the results of four methods (Table 13), and showed that at a critical value of the ionic radius (about 1.6 Å), the ionic field no longer holds the water in contact with the ion, losing it through thermal motion to the field of the surrounding water structure. The results indicate that if the primary hydration shell of an ion is sufficiently stable, it shows an increasing tendency to remain in the diffuse layer, rather than be bound at the surface.

The analysis of ion-surface interaction given above arises from the proposed mechanism that ion binding occurs at discrete sites on the clay mineral surface, with the result that the charge at the O.H.P. - diffuse layer boundary can no longer be treated as a homogeneous charge

Specific adsorbability plotted against ionic radius for monovalent Fithian illite systems (logarithmic scale) - based on $A_o = 110\,m^2/g$.

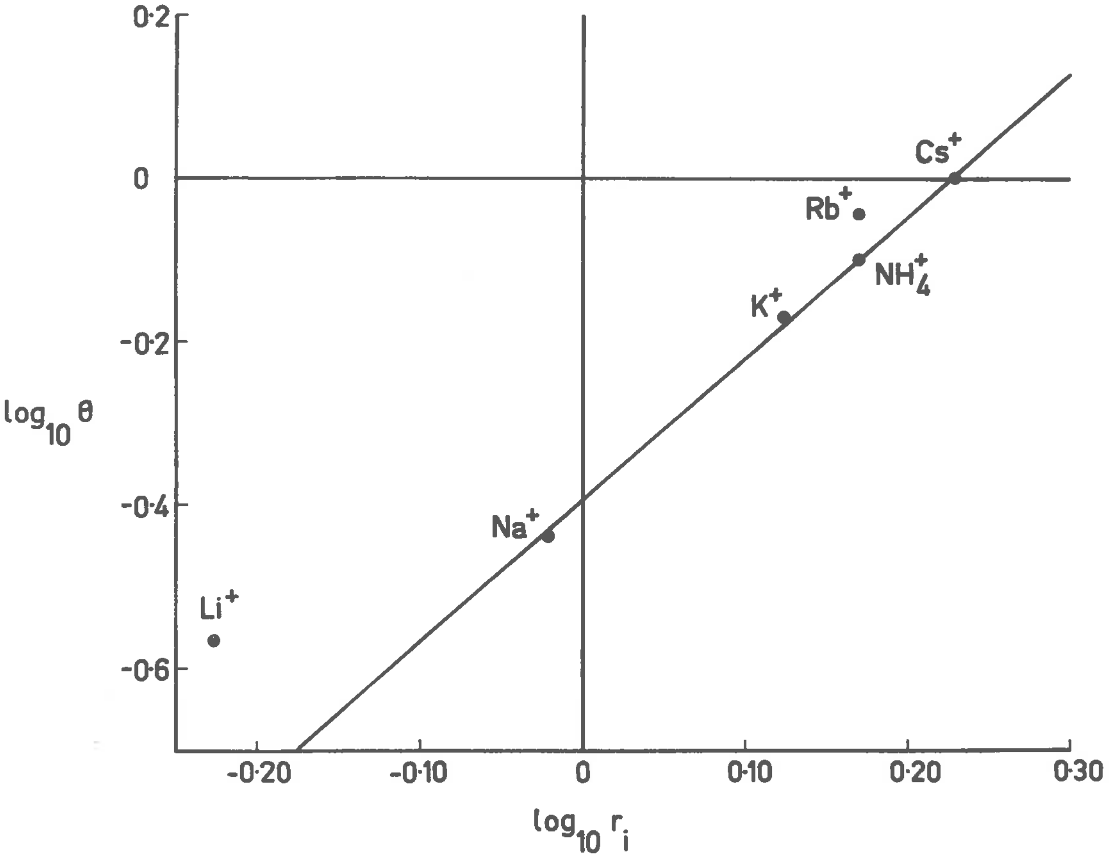


FIGURE 17.

TABLE 13

PRIMARY HYDRATION NUMBERS OF ALKALI METAL CATIONS

(BOCKRIS, 1949)

Cation	Ionic Radius (Å)	Hydration Number
Li	0.60	5
Na	0.95	5
K	1.33	4
Rb	1.48	3
Cs	1.69	0

smeared over the entire boundary. The clay surface itself is envisaged as possessing a uniform surface density of charge, resulting from isomorphous replacement. However, because certain parts of the surface bind ions by ion pairing, these areas are effectively uncharged. The results further suggest that the surface is composed of a mosaic of charged and uncharged areas(sites), and that at the defined reference concentration the charged areas possess the same charge density as that of the fully ionized clay surface.

B. Chloride Exclusion by Wyoming bentonite.

1. General Results.

The chloride exclusion data for Li^+, Na^+, K^+, NH_4^+ and Cs^+ Wyoming bentonite are plotted in Figs. 18 and 19, according to Schofield's negative adsorption equation (39). The surface areas obtained ranged from 625 $m^2/g.$ for the Li^+ system down to 156 $m^2/g.$ for the Cs^+ system. The total expected surface area of 700 $m^2/g.$ was not measured in any system. The reason for this will be discussed later.

The intercepts of the chloride exclusion curves on the $\frac{q}{\sqrt{z\beta C_0}}$ axis are merely extrapolations of the behaviour at low electrolyte concentrations, where double layers exist. However, as shown by Posner and Quirk (1964) chloride exclusion at high electrolyte concentrations is no longer a linear function of $\frac{1}{\sqrt{C_0}}$, and the curves tend to run approximately parallel to the x-axis, at volumes corresponding to the regions from which electrolyte is excluded.

Chloride exclusion by monovalent Wyoming bentonite systems.

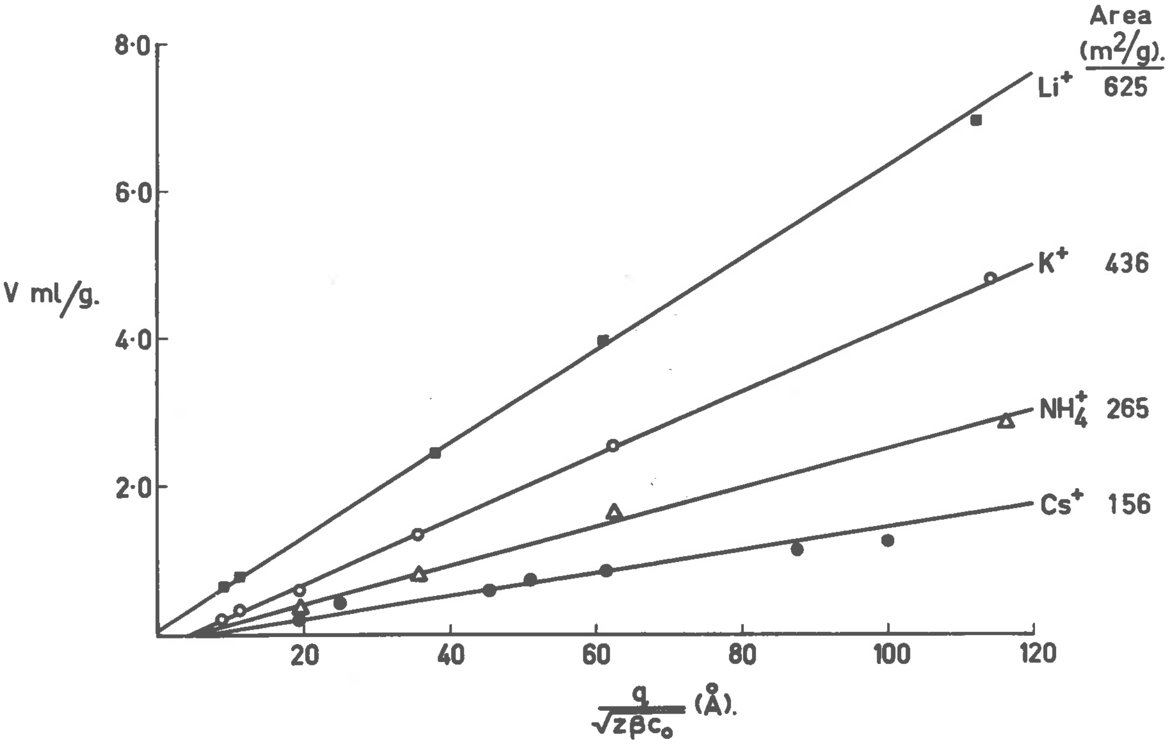


FIGURE 18.

Chloride exclusion by sodium Wyoming bentonite.

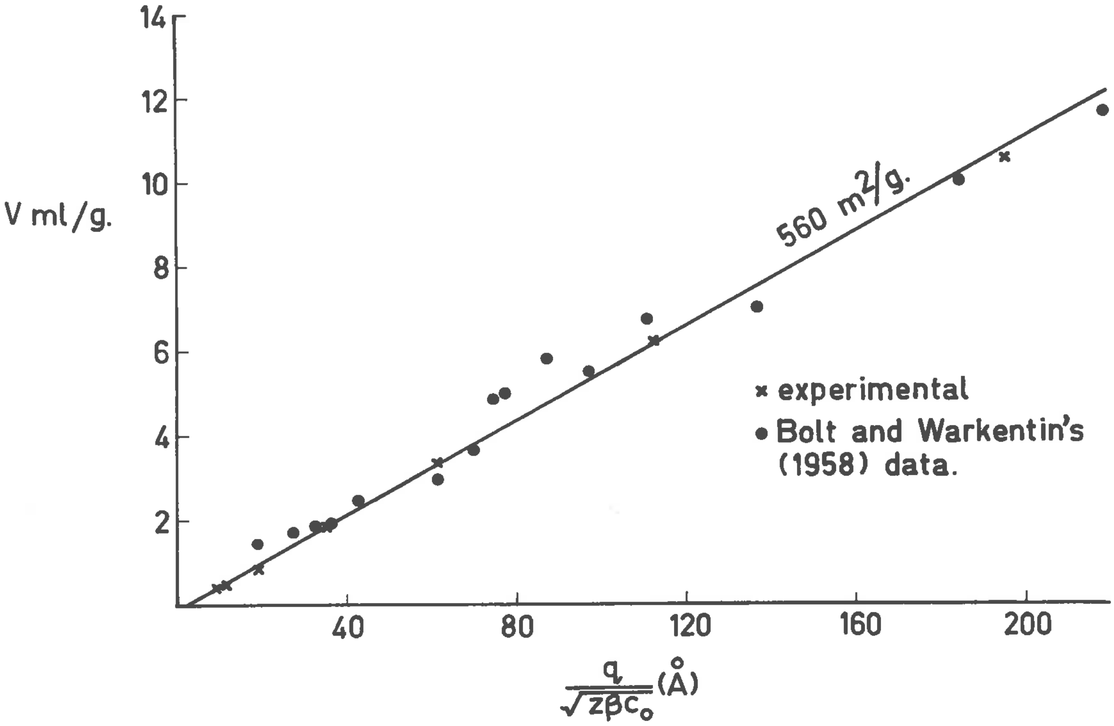


FIGURE 19.

2. Interpretation by General Theory of Binding.

The chloride exclusion data for the monovalent Wyoming bentonite systems are plotted in Fig. 20 according to the general binding equation developed in interpreting the Fithian illite results. The line of best fit through all points may be represented by the following equation

$$r\theta = -6.16 + 0.46r^2 \tag{90}$$

The theoretical equation was also solved for Wyoming bentonite at the reference concentration, which in this instance is 0.292 M. At this concentration the areas of the ionic atmospheres of the free ions are equal to the area of surface associated with each charged site, viz. 127.7 Å^2. The theoretical equation obtained, neglecting desolvation is

$$r\theta = -2.46 + 0.27r^2 \tag{91}$$

The discrepancy between the intercepts could be accounted for by invoking about 5 per cent desolvation of the bound cations. However, the discrepancy in slope may be accounted for in the following way. The equations of the lines drawn through the various points (Fig. 20) are as follows:

Li^+, Na^+ $\quad r\theta = -1.43 + 0.15\ r^2$ . . . . (92)

Li^+, Na^+, K^+ $\quad r\theta = -2.78 + 0.23\ r^2$ . . . . (93)

Na^+, K^+ $\quad r\theta = -3.25 + 0.27\ r^2$ . . . . (94)

Binding of monovalent cations on Wyoming bentonite.

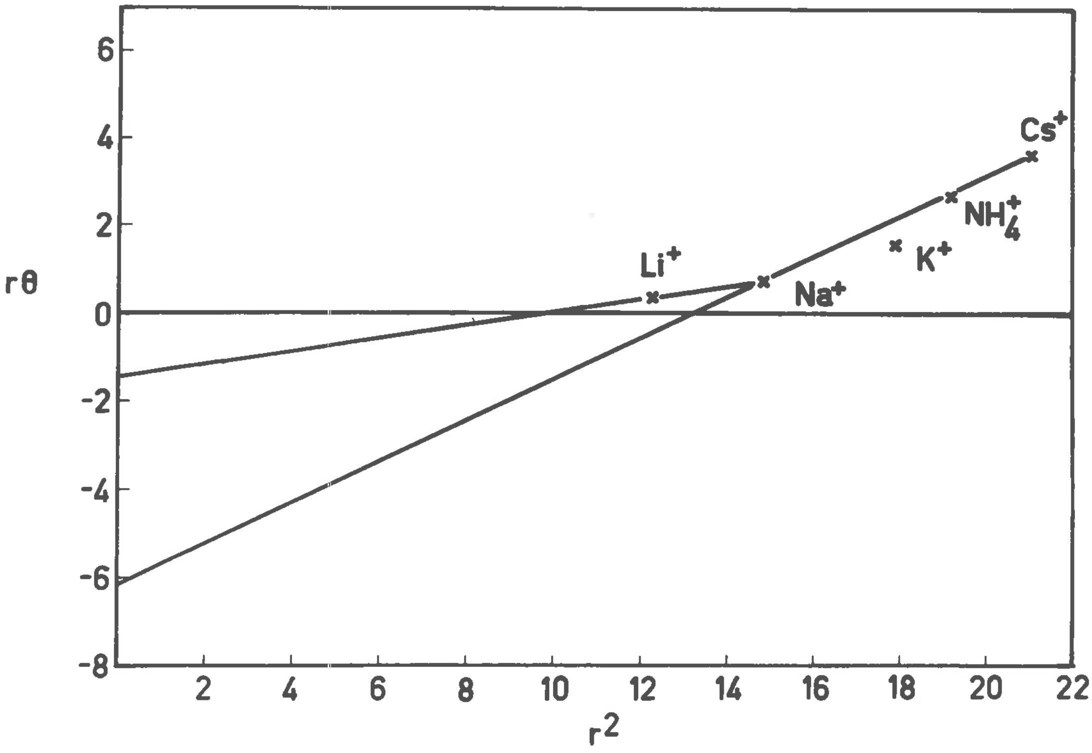


FIGURE 20.

There is seen to be an increase in slope as the hydrated ionic radius increases, suggesting that the binding energy increases as the ionic radius increases. For ions with a greater radius than Na^+ (or possibly K^+) increasing deviations from theory occur, consistent with some other factor influencing binding and causing the binding energy to increase more rapidly than expected.

It is also noteworthy that the cations showing deviation from the expected behaviour also shown an increasing tendency to cause the montmorillonite lamellae to associate, giving discrete plate separations of one or two water layers, rather than a large interlamellar spacing which varies continuously with electrolyte concentration. Thus over the concentration range 0.5 ⟶ 0.003 N used in these experiments, Cs^+ lamellae have a fixed basal spacing of 13.3 Å, NH_4^+ 15.0 Å, while K^+ ranges from large interlamellar separations down to a fixed 15.3 Å spacing. Li^+ and Na^+ montmorillonite, on the other hand, show basal spacings varying from about 36 Å to 230 Å (Norrish, 1954) over the same concentration range. Thus the plates are separated either by a large distance in which the diffuse double layers show some interaction, as in the case of Li^+ and Na^+, or else by a small distance only a few water molecules thick in which diffuse layers are not developed, e.g. Cs^+, NH_4^+.

The association of the montmorillonite clay plates in the form of crystals may be another reflection of the strong cation association with the clay surface, previously discussed by Mattson (1929), Davis (1942) and Deshpande and Marshall (1959, 1961). The exchangeable cations of a given plate increase their extent of association either through a decrease in electrolyte concentration or by replacement with a cation of greater radius during preparation of the homo-ionic clay systems. Thus although an increase in electrolyte concentration causes an increased dissociation of ions into the diffuse layer where they possess normal mobilities, the extent of their ionic atmospheres is reduced, and the diffuse layer ions, although there are more of them, are found closer to the surface. As the process continues, there is probably a co-operative association of the ions due to a changing dielectric constant, reduction in image force and hence an increase in the attractive energy between the platelets. Thus the plates because of their small size and consequent ability to move under small forces, will approach one another until by sharing the charge the double layers are eliminated, and a one, two, three or four water layer separation is obtained. It is considered that this sharing of charges between the plates effectively brings about complete ion association on the internal crystal surfaces, under these conditions. The approaching montmorillonite plate is effectively behaving as a large mobile anion, giving a more efficient neutralization of the mobile cations. This situation is not present in the Fithian illite systems because of the relatively large crystal sizes and lack of small mobile platelets.

It is now important to consider the effect of a plate on its neighbour. If the association of the cation with the clay surface is weak, then it is conceivable that as a result of association between adjacent faces of a pair of parallel plates, there will be an increase in dissociation on the other sides. This would arise because of a decrease in double layer interaction with the next neighbour as a result of the increased distance of separation. Further, since the cations in the whole system must be in equilibrium, increased ion association on one side of a plate which is promoted by the approach of another plate, would lead to an increased dissociation on the other side of the plate. Even when diffuse double layers are interacting the stronger the interaction the greater will be the association of the interlayer exchangeable cations for the opposed surfaces. Thus, as double layer interaction increases it is proposed that there is an increase in ion binding on each surface, rather than interaction between the ionic atmospheres of the free ions. This withdrawal of ions into the adsorbed region may be envisaged as the first step in the formation of clay crystals from single independent platelets.

In the case of strong interaction between the cation and the clay surface, the collapse of adjacent plates will be transmitted, until several clay platelets come together to form a large crystal. The size of this crystal may be governed by the position of the equilibrium between undissociated and dissociated cations. Again, it might be expected that the cations on the external surfaces may be dissociated to an extent such that the full surface area may be measured. Where the surface-cation association is strong, the crystals might be expected to be large and to have a fairly uniform size distribution. Where the association is of intermediate strength, a mixture of both large diffuse layer spacings and small 2, 3 or 4 water layer spacings may be expected, even in the same crystal. Alternatively there may be a range of crystals of different sizes which, however, still obey the association-dissociation equilibrium. In the case of weak association, a distribution of large double layer spacings around a mean would be expected. The X-ray diffraction measurements of Norrish (1954) demonstrated that this is the case.

It is of interest to note that there is good agreement between the B.E.T. nitrogen adsorption area (146 m^2/g.) and the chloride exclusion area (156 m^2/g.) of Cs^+ Wyoming bentonite. This suggests that the number of exchangeable cations dissociated from the external crystal surfaces is sufficient for the full surface area to be measured by chloride exclusion. The constancy of the Cs^+ Wyoming bentonite areas suggests that the large uniform crystals tend to behave as separate entities, showing little tendency to collapse together and form larger crystals on drying. In the other montmorillonite systems the chloride exclusion areas are considerably greater than those of Cs^+ Wyoming bentonite, while the B.E.T. nitrogen adsorption areas are much smaller (Table 14). The nitrogen surface areas are less than those of Cs^+ Wyoming bentonite, because drying causes further condensation of small mobile platelets which is not possible with Cs^+. In the Li^+ and Na^+ systems where the mobile plates are separated by distance approaching $^4/K$, drying would tend to be uniform, all surfaces being virtually equivalent. The mobile plates would tend to orientate

TABLE 14

SURFACE AREAS OF MONOVALENT WYOMING BENTONITES

Saturating cation	Chloride exclusion area ($m^2/g.$)	Nitrogen adsorption area ($m^2/g.$)	
		Edwards	Mooney, Keenan and Wood
Li^+	650	66	41.0
Na^+	560	46	33
K^+	436	64	48.5
NH_4^+	256	59	-
Cs^+ (ex Na^+)	156	146	108 *
Cs^+ (ex Ca^{++})		135	

* Barrer and Reay (1958) reported a N_2 adsorption area of 141 $m^2/g.$ for Cs^+ Wyoming bentonite.

themselves in a parallel manner, under the influence of the drying process. The collapse of one plate on to its neighbour would thus be transmitted more readily through such a system of plates than in the Cs$^+$ system where relatively large crystals have to orientate themselves parallel to one another before further condensation can occur. NH$_4^+$ montmorillonite in suspension may only possess an average of about three plates per crystal. Thus, on drying it will be easier to orient and condense NH$_4^+$ crystals than the larger Cs$^+$ crystals.

The analysis of the chloride exclusion results for Na$^+$ Wyoming bentonite, to be discussed below in terms of a parallel plate model with the plates separated by a distance $^4/K$, showed that the area to be expected is considerably less than the thoretical 700 m^2/g. because of the persistence of the association of the clay plates in the form of crystals. This association is weaker than that in the Cs$^+$, NH$_4^+$ and to a lesser extent K$^+$ systems where fixed spacings occur, and all the interlayer cations are associated. However, in all systems, the number of ions dissociating from the external crystal surfaces is sufficient for the full area to be measured by chloride exclusion techniques.

In much the same way as for the Fithian illite systems, it would appear that the position of the "bound" cation may vary with the cation itself. Thus bound sodium ions may occur either at the surface as Fuoss ion pairs, or removed one, or two water layers from the charged surface because the greatest spacing for limited crystalline swelling is 18.5 Å (Posner and Quirk, 1964). In Cs$^+$ Wyoming bentonite, where a fixed 13.3 Å spacing is obtained, caesium ions are either bound at the surface or as modified Bjerrum ion pairs consistent with a plate separation approaching 4 Å. Probably the tendency is for Cs^+ ions to be bound in the I.H.P., while the more hydrated ions show increasing tendencies towards association in the O.H.P., or even two water layers removed from the surface. The associated interlayer cations in K^+ and NH_4^+ Wyoming bentonite would tend to occur in an O.H.P. removed one water layer from the surface, as well as in the I.H.P. directly at the surface. Walker (1949, 1951) considered that the exchangeable interlayer cations merely line up in the median plane between two opposed plates. However, it seems much more feasible that they will exist at the surface as well as in the median plane, which will have the special significance that it represents a modified O.H.P. at which Bjerrum-type ion pairing is occurring.

Summarizing, it is believed that the presence of the small mobile montmorillonite plates promotes through a co-operative energy mechanism an increased association of the larger, less hydrated ions for the surface. This condition is absent in the Fithian illite systems. Thus the lower part of the $r\theta$ v r^2 curve for the more hydrated ions approximates the theoretical requirement since the plates are widely separated, while the upper part shows an increasing deviation due to the co-operative interaction effect between plates which increases with increasing ion size and is manifest as an increased attraction between the cations and the plates.

3. Association of Clay Plates in the Form of Crystals.

The total surface area of Wyoming bentonite can be calculated from crystallographic data. The basal plane area per unit cell is 2 x 46 Å^2, and the unit cell weight is 765. The basal plane area is therefore 725 m^2/g., and since the cleavage face dimensions (1,000 Å) are large compared to the thickness (10Å), the contribution of the edge area can be neglected. As previously noted, the sample used for this work contains 2%-3% quartz, so that 700 m^2/g. would appear to be the most appropriate value to use in discussing the present results.

The results reported in Fig. 19 for sodium montmorillonite are in general agreement with those reported by Bolt and Warkentin (1958). The surface area of 560 m^2/g. obtained from the slope of the line in Fig. 19 is somewhat less than the 700-800 m^2/g. reported earlier by Bolt and Warkentin. However, it can be seen that their results lie near the line of best fit to the results reported here, and, in any case, the line of best fit to their results would give a surface area less than 700 m^2/g. The general concordance of the two sets of data leads to the conclusion that the full surface area of 700 m^2/g. is not obtained from negative adsorption measurements on sodium montmorillonite.

Bolt and Warkentin attributed this deviation to the presence of positive charges, but an alternative explanation is possible based on the association of the clay plates in crystals, presumably because of ion association as discussed earlier. Norrish and Quirk (1954) using

X-ray diffraction observed that sodium montmorillonite immersed in 0.31 N NaCl gave a d(001) basal spacing of 40 Å, while Norrish (1954) showed that in more dilute NaCl solutions the d(001) spacing increased linearly with respect to $\frac{1}{\sqrt{C_o}}$ where Co is the bulk electrolyte concentration. The presence of basal reflections corresponding to elementary silicate sheet separations of greater than 100 Å indicates the persistence of the crystals.

The association of clay plates in crystals leads to the possibility of restrictions in double layer development between opposed plates, owing to the interaction of opposed double layers. In discussing the conditions under which Schofield's equation (39) is applicable, it was shown that the plate separation had to be at least four times the value of the negative adsorption depth $\frac{q}{\sqrt{z\beta C_o}}$ (i.e. $^8/K$) for complete double layer development to occur. However, it can be seen in Table 15 that, in fact, $\frac{q}{\sqrt{z\beta C_o}}$ gives a good approximation to the film thickness (half distance of plate separation) derived from X-ray data. This agreement would be even closer if allowance was made for the factor $\frac{4}{z\beta\Gamma}$ (≈ 3 Å). Hence, it appears that double layer development is restricted because the plate separation is approximately $^4/K$, instead of $^8/K$ as required by Schofield's theory.

To see whether the low value of 560 m^2/g. obtained from the slope in Fig. 19 could be explained by this restriction in double layer development, an analysis was conducted using equations (10), (12), (42) and (43). The calculations were based on plate separations of $^4/K$. Values of α_- for single plates and α'_- for interacting plates, together

TABLE 15

Comparison of Film Thickness (X) and Negative Adsorption "Depth" $\left(\frac{q}{\sqrt{z\beta C_o}}\right)$ for Sodium Montmorillonite in NaCl.

Concn (C_o)	$\frac{1}{\sqrt{C_o}}$	Intracrystalline d(001) spacing	Film Thickness* (X)	$\frac{q}{\sqrt{z\beta C_o}}$
meq./ml x 10^{-2}		Å	Å	Å
25	2	45	18	12
11	3	55	23	18
6.3	4	67	29	25
4.0	5	78	34	31
2.8	6	89	40	37
2.0	7	100	46	43
1.0	10	133	63	61

$* X = \frac{d(001) - 10}{2}$ See Norrish (1954) with the percentage underestimate of chloride deficit arising from double layer interaction under the stated conditions are given in Table 16. It is to be noted that the exclusion of chloride is given by the general relation

$$\Gamma_- = \alpha_- \Gamma \tag{95}$$

The application of the corrections in Table 16 to experimental results will depend upon the division of total surface area between external and internal crystal surface. Expected chloride exclusion volumes were calculated for external surface areas of 50, 100, 200 and 700 $m^2/g.$, this last condition occurring when the crystals have broken down to give independent 10 Å platelets. The calculations were made on the basis that the full exclusion takes place from the external surfaces, and that the remainder of the 700 $m^2/g.$ is internal crystal surface subject to restriction in double layer development.

The experimental results included in Fig. 21 support the view that the low value of 560 $m^2/g.$ can be attributed to incomplete chloride exclusion from internal crystal surfaces. If complete dispersion of the crystals into elementary silicate sheets occurs, and enough exchangeable cations are dissociated from the surface, the experimental points ought to lie on the line for 700 $m^2/g.$ The experimental points, particularly at low concentrations (the value obtained at 0.0001 N was 34.7 ml/g. compared with the expected 42.7 ml/g. for complete

Expected exclusion volumes for sodium Wyoming bentonite crystals with external surface areas of 50, 100, 200, and 700 m^2/g. These volumes take into account the interaction between opposed double layers on the internal crystal surfaces.

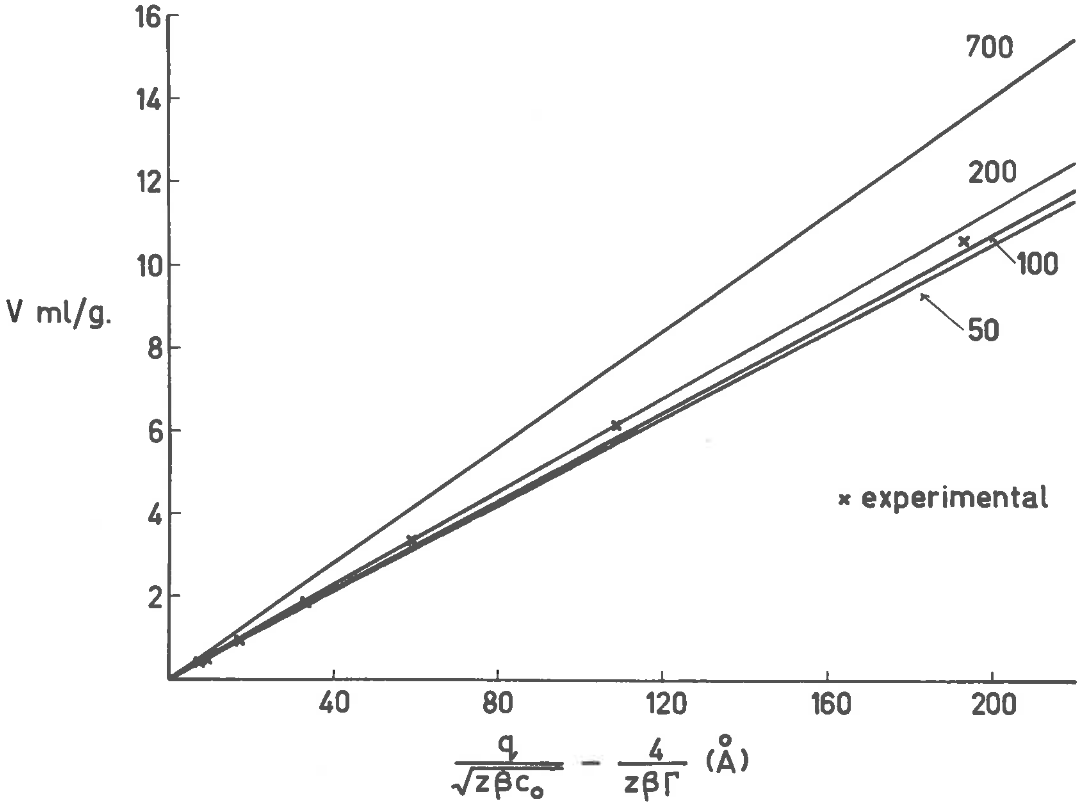


FIGURE 21.

TABLE 16

Percentage Underestimate of Chloride Deficit due to Restriction in Double Layer Development when opposed Plates are a distance $^{4}/K$ apart.

NaCl concn. meq./ml.	Single Plate		Interacting Plates			Percentage restriction
	ψ_o (mV)	α_-	ψ_o (mV)	ψ_d (mV)	α'_-	$\frac{\alpha_- - \alpha'_-}{\alpha_-}$
1.0	-47.42	0.2813				
0.1	-98.25	0.1252	- 99.23	-17.24	0.1101	12
0.01	-155.5	0.0441	-157.2	-25.98	0.0340	23
0.003	-185.9	0.0246				
0.001	-213.6	0.0144	-215.8	-29.70	0.0105	27
0.0001	-306.8	0				

dispersion) are well below that to be expected for 700 m^2/g. The results are not inconsistent with an external surface area of 100 - 200 m^2/g., i.e. there would be on an average 3-7 elementary silicate sheets in each crystal.

If the nitrogen surface area of Cs^+ Wyoming bentonite is a reflection of the ultimate crystal size in suspension, the agreement between that area and the chloride exclusion area provides strong evidence that enough ionic atmospheres are formed around free exchangeable ions for the maximum external exclusion volume to be measured. X-ray measurements in water and dilute CsCl solutions showed a d(001) spacing of 13.3 Å which decreased to 12.3 Å when the CsCl concentration was greater than 0.2 N. Since the Cs^+ montmorillonite platelets are so strongly associated in the form of crystals under all conditions, it is reasonable to assume that practically no bulk electrolyte ions, either Cs^+ or Cl^- penetrate the interlamellar regions. The internal surface charges are simply balanced by the associated interlayer cations.

A further point of interest may be found in comparing more closely the nitrogen surface areas of the homoionic Wyoming bentonite systems (Table 14). In discussing the relationships of these areas in the previous section on binding, the differences in area were attributed to differences in crystal size. However, the possibility of interlamellar penetration of nitrogen into the crystal lattice must be considered. For this to occur a d(001) spacing of about 12.3 Å would be required.

Mooney, Keenan and Wood (1952) reported a minimum spacing of

12.4 Å for caesium montmorillonite (cf. 12.3 Å; this thesis). However, on drying a sample of the caesium clay over P_2O_5, in vacuo, at 110°C an irrational series of d(001) spacings of 10.7 Å was obtained. This may be attributed to migration and partial accommodation of the exchangeable caesium ions in the hexagonal holes in the surface oxygen layers, i.e. keying. Hofmann, Endell and Wilm (1933) considered that these holes were 3.3 Å in "free diameter", a term denoting that diameter not occupied by the even periphery of the surrounding oxygen atoms. Barrer and Reay (1958) showed that ions up to 2.4 Å in diameter could be totally accommodated below the sheet surface. Under these conditions a d(001) basal spacing of about 9.6 Å would be expected. It seems most improbable that the caesium ion of diameter 3.38 Å could be accommodated completely within a hexagonal hole. Thus, a partially buried caesium ion directly opposed by a surface oxygen atom would be expected to give a d(001) spacing of about 10.6 Å. The value of 10.7 Å reported here is in good agreement. Thus, there are no grounds for attributing the much larger surface area of Cs^+ Wyoming bentonite to the interlamellar intercalation of nitrogen. The differing nitrogen surface areas are simply measures of the overall crystal size on drying and outgassing at 300°C, and reflect the tendency of the montmorillonite lamellae to collapse together during this drying process.

C. Chloride Exclusion by Grundite Illite.

The chloride exclusion data for Na^+ and Cs^+ Grundite illite are plotted in Fig. 22, according to Schofield's negative adsorption

Chloride exclusion by sodium and caesium Grundite illite.

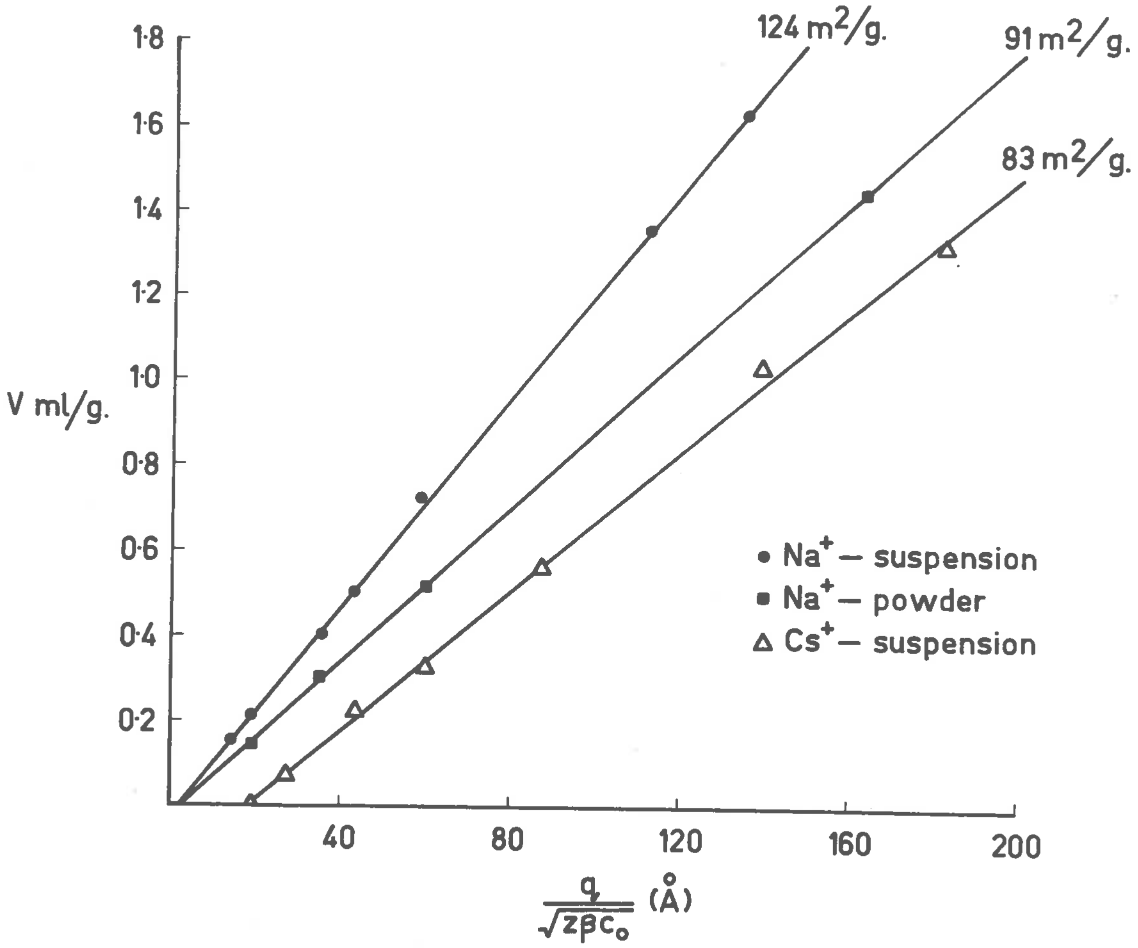


FIGURE 22.

equation (39). The data have also been plotted in Fig. 23, according to the general theory of binding. For comparison the curves representing the Fithian illite and Wyoming bentonite results have also been included. As would be expected, the interstratified Grundite illite shows some characteristics of each of the other two systems.

The Na^+ Grundite illite results in particular are extremely interesting. The low temperature nitrogen surface area was 104 m^2/g. The suspension phase gave a surface area of 124 m^2/g., indicating that the mineral is interstratified, while chloride exclusion measurements on the powder phase gave an area of only 91 m^2/g. Calculating $r\,\theta$ values on the basis of $Ao = 161\ m^2/g$. (CPB area of Greenland and Quirk, 1962), the suspension results lie very close to the Wyoming bentonite results, while the powder results consistent with a greater degree of ion binding at the surfaces lie on the Fithian illite line. This indicates that either full interstratification is not reached in the powder system, and that virtually all the exclusion is occurring from the external crystal surfaces or, alternatively, the numbers of dissociated ions in the interstratified regions may be much less than the numbers in the corresponding Wyoming bentonite systems. However, in the suspension phase there is a definite and significant contribution due to double layer development in the interstratified regions. However, the area A_o of 161 m^2/g. is not obtained because of double layer interaction in the interstratified regions allied with incomplete exclusion from the external surface areas where not enough ions have dissociated to allow the full external area to be measured.

Binding of monovalent cations on Grundite illite.

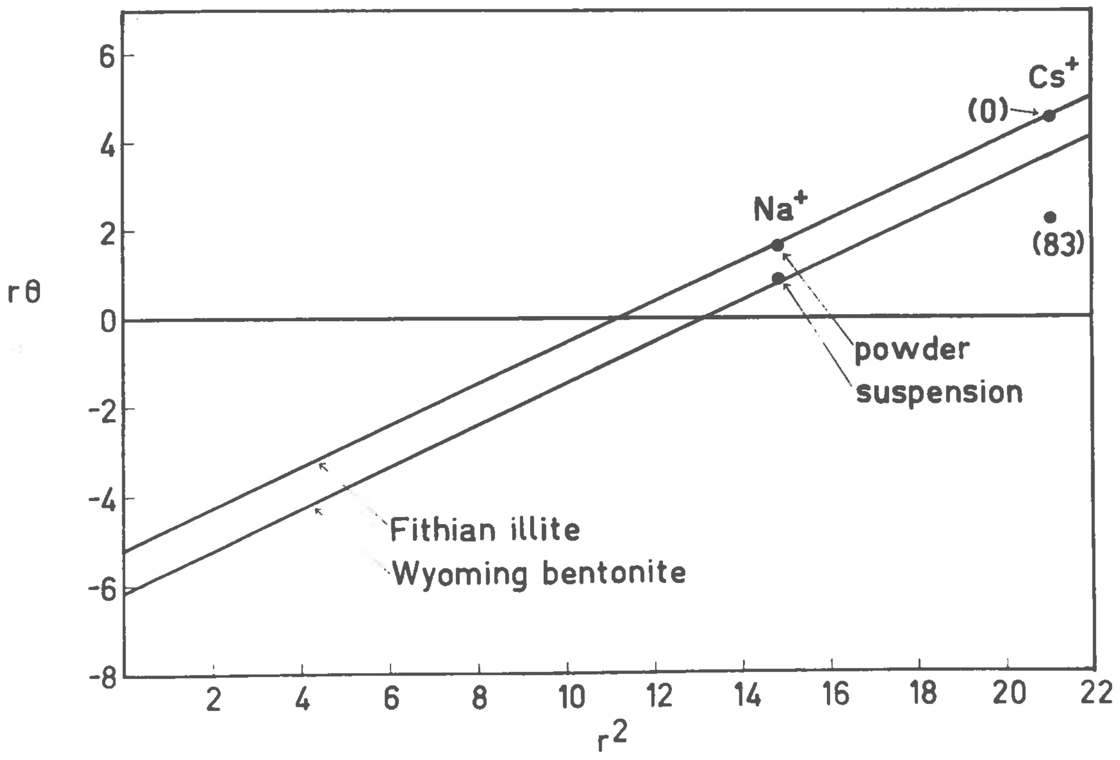


FIGURE 23.

Chloride exclusion measurements from Cs^+ Grundite illite suspensions showed the interesting phenomenon of zero exclusion at electrolyte concentrations > 0.1 N, followed at lower electrolyte concentrations by exclusion consistent with a surface area of 83 m^2/g. The nitrogen surface area was 103 m^2/g. Zero exclusion at high electrolyte concentrations indicates that the exchangeable cations are completely localized at the external surface exchange sites. Furthermore interlayer exchangeable Cs^+ ions will be associated with the internal surfaces in the same manner as occurs in the Cs^+ Wyoming bentonite system. A fixed spacing would tend to exist across these interstratified regions when the clay is caesium saturated. Thus chloride exclusion from an area of 83 m^2/g. at low electrolyte concentrations must be attributed to dissociation of exchangeable cations from the external surfaces of Grundite illite. This further suggests the presence of some low charge density areas on the external crystal surfaces. However, the fact that not enough Cs^+ ions dissociate to allow the full surface area to be attained suggests either that the surface is a mosaic of high and low charge density regions, or possibly that the external crystal surfaces carry a uniform charge density which lies between that of Wyoming bentonite and Fithian illite. This view is in agreement with the suggestion of Greenland and Quirk (1962) that "the surfaces of micaceous crystals may have properties different from those indicated by the bulk composition, and it may be speculated that the external surfaces of many interstratified illites may be more like montmorillonite than mica surfaces." This suggestion was based on surface densities of charge calculated from CPB adsorption measurements on Sarospatak illite and Grundite illite. These data are presented in Table 17, along with similar data for Fithian illite, and Willalooka illite which are not interstratified. It can be seen that the surface density of charge of Sarospatak illite, based on CPB adsorption is even less than that of Wyoming bentonite, while that of Grundite illite is intermediate. Thus, it is not surprising that Grundite illite shows certain characteristics of both low and high surface charge density clay minerals.

The agreement between the nitrogen surface areas of Na^+ (104 $m^2/g.$) and Cs^+ (103 $m^2/g.$) Grundite illite discounts the possibility of crystal size differences for the various saturating cations.

D. Chloride Exclusion by Milford Saponite.

Chloride exclusion measurements made on Na^+ and Cs^+ Milford saponite, plotted according to Schofield's equation in Fig. 24, resulted in surface areas of 740 $m^2/g.$ and 66 $m^2/g.$ respectively. These data have also been plotted in Fig. 25, according to the general binding theory that has been developed in this thesis.

The surface area of Na^+ Milford saponite was measured by CPB adsorption from aqueous solution and shown to be 800 $m^2/g.$ This value agrees quite well with the surface area of 762 $m^2/g.$ calculated from the crystallographic data of Norrish (unpublished). This area agrees with the 760 - 780 $m^2/g.$ calculable from the crystallographic data of Ross and Hendricks (1945) and Weiss, Koch and Hofmann (1955) for a

Chloride exclusion by sodium and caesium Milford saponite.

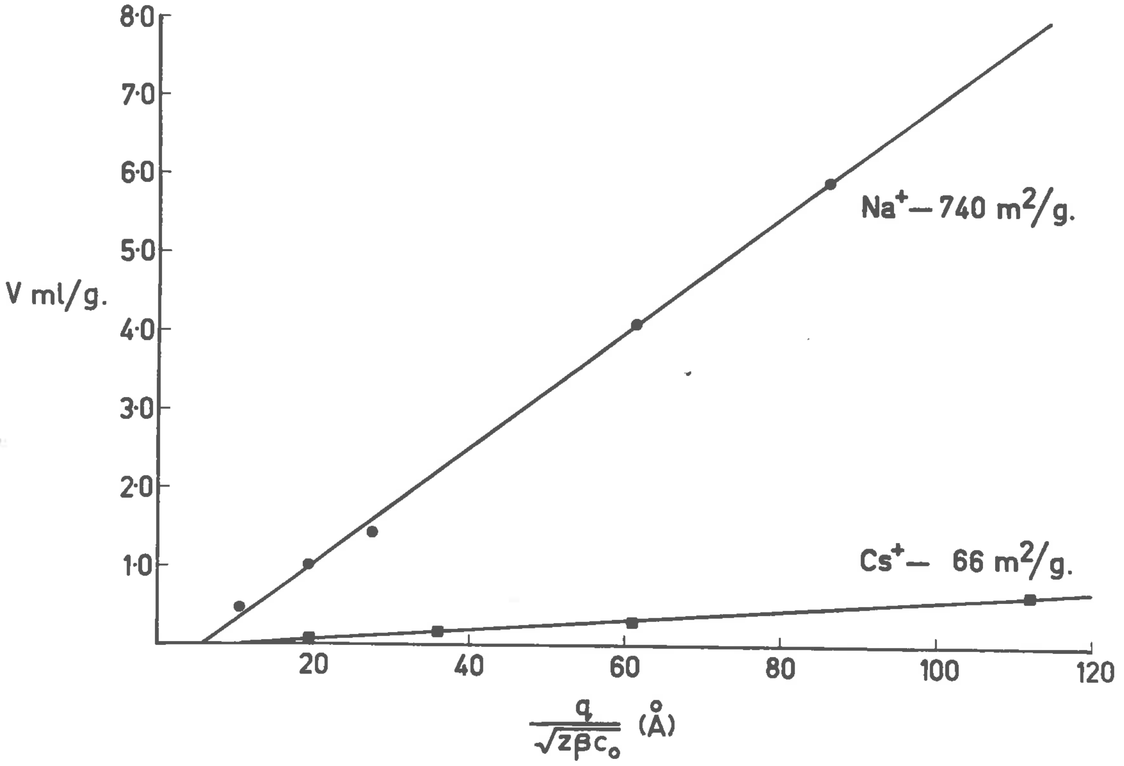


FIGURE 24.

Binding of sodium and caesium ions by Milford saponite.

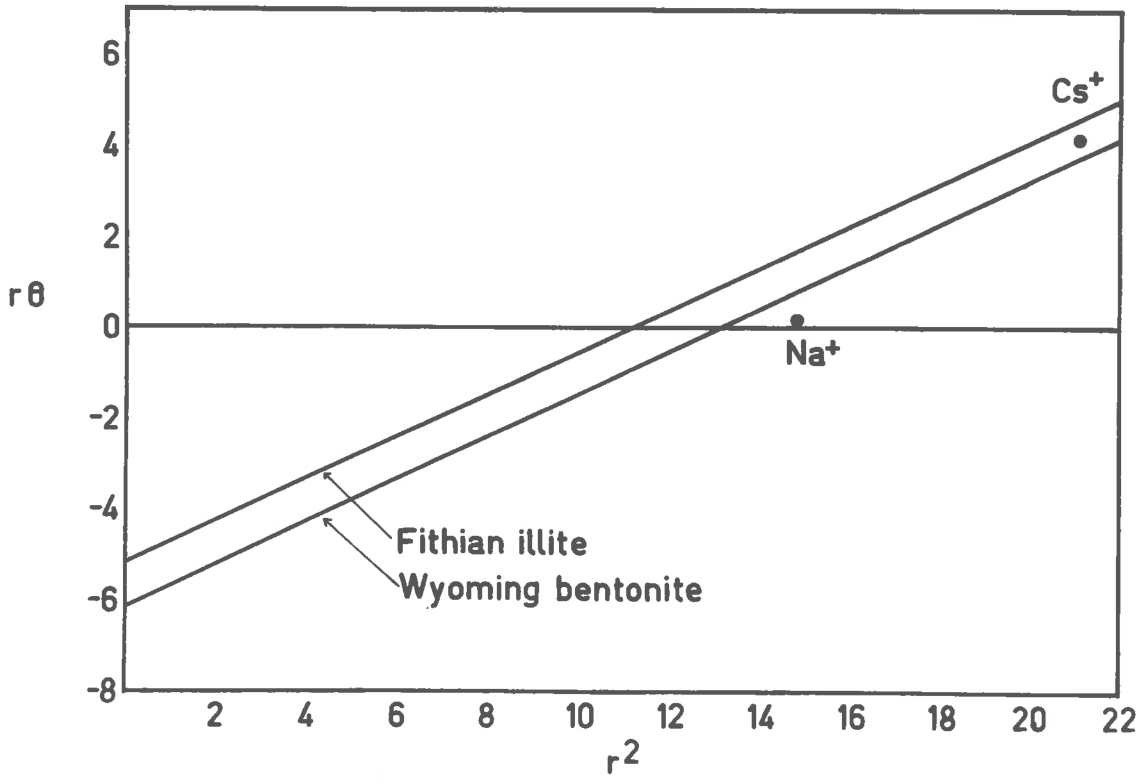


FIGURE 25.

TABLE 17

SURFACE CHARGE DENSITIES OF ILLITES CALCULATED FROM NITROGEN AND CPB AREAS

(Greenland and Quirk, 1962)

Source	Surface area m^2/g.			Area ($\mathring{A}^2$) per charge based on	
(a) **Illites**	N_2	CPB	meq./g.	N_2 area	CPB area
Fithian	93	96	0.26	60	60
Willalooka	132	131	0.41	54	54
(b) **Interstratified Illites**					
Grundite	105	161	0.30	59	89
Sarospatak	43	152	0.16	45	158

range of saponites. Thus the chloride exclusion area of 740 m^2/g. indicates that the individual plates are highly dissociated, and that virtually unimpeded double layer development occurs on both external and internal crystal surfaces. In fact, Na^+ Milford saponite may be considered to be very near complete dispersion into independent plates. Furthermore, the nitrogen surface area of 9.4 m^2/g. indicates that extremely large crystals are present under the conditions in the nitrogen adsorption apparatus. The virtual independence of the plates (within a crystal) in the suspension phase, suggests that on slow drying of this phase, many plates would tend to orientate and collapse together, so forming extremely large crystals. The mechanism of this behaviour has been considered in discussing the Wyoming bentonite results.

Although enough exchangeable ions are dissociated from all the crystal surfaces of Na^+ Milford saponite to allow an area of 740 m^2/g. to be measured, the chloride exclusion results for the Cs^+ clay are very different. The chloride exclusion area of 66 m^2/g. is considerably less than the nitrogen adsorption area of 152 m^2/g. for Cs^+ Milford saponite, indicating that not enough exchangeable ions dissociate to allow the full external area to be determined. Cs^+ saponite shows a fixed d(001) basal spacing of 12.3 Å, under which conditions all the exchangeable interlayer cations will be associated with the internal crystal surfaces by ion pairing. In this way, Cs^+ saponite resembles Cs^+ montmorillonite. However, the lower d(001) spacing for the saponite may presumably be attributed to its higher surface charge density (Table 18). Both Cs^+ saponite and Cs^+ montmorillonite show the same type of crystal behaviour; both possess stable crystals of

TABLE 18

EFFECT OF SURFACE CHARGE DENSITY ON MAXIMUM d(001) SPACING OF CAESIUM CLAYS.

Clay Mineral	Exchange capacity meq./g.	σ esu/cm^2	Maximum d(001) Å
Pyrophyllite*	-	0	No interlayer cation No swelling
Montmorillonite	0.93	3.8×10^4	13.3
Saponite	1.23	4.7×10^4	12.3
Vermiculite*	-	6×10^4	12.0
Illite	0.30	8×10^4	10

* From Norrish (1954)

about 5 plates, and these crystals tend to exist as separate crystal entities, even on slow drying. However, the major difference in the suspension behaviour of the two caesium clays would appear to lie in the relative dissociation of the exchangeable cations from external crystal surfaces. Thus, not enough exchangeable caesium ions dissociate from the external surfaces of saponite to allow the full area to be measured, as is the case with montmorillonite. On the other hand this dissociation may be compared with the Fithian illite system, where no exchangeable caesium ions are dissociated. Thus there is a definite relationship between charge density and the dissociation of exchangeable caesium ions from external crystal surfaces; the higher the charge density, the smaller is the number of caesium ions that may dissociate, and thus the bigger the reduction in area from the expected.

Grim (1953) suggested that the position in the clay mineral lattice at which isomorphous replacement occurred could affect the bonding force of exchangeable cations to the surface. Thus, he considered that since substitutions in the octahedral sheet would act through a greater distance than the charges resulting from substitutions in the tetrahedral sheet, the force by which cations would be held at the surface would be much smaller in the case of octahedral replacement. However, comparison of the results for Wyoming bentonite, in which the charge is octahedral in origin and Milford saponite, in which the charge is tetrahedral in origin does not provide any definite evidence, one way or the other, that the site of the charge affects the energy of ion binding. Certainly, caesium ions are more associated on the external surfaces of the saponite than montmorillonite, but they are not as completely associated as on the Fithian illite surfaces, where the charge once again is tetrahedral in origin.

II. DIVALENT ION SYSTEMS

A. Chloride Exclusion by Fithian Illite.

Surface areas obtained from chloride exclusion measurements on Mg^{++}, Ca^{++}, Ba^{++} and Sr^{++} Fithian illites are presented in Table 19, together with the surface areas obtained from low temperature nitrogen adsorption. The most interesting feature of these results lies in the extremely low surface areas obtained from chloride exclusion. In view of the results for the binding of monovalent cations on the surfaces of Fithian illite it is not surprising that the divalent ions, as a whole, are bonded even more strongly. The extremely efficient binding mechanism in these systems is due to the greater electrostatic forces between divalent ions and the charged surface.

The energetics of the systems would suggest that the bound divalent cations would tend to take up positions midway between two adjacent charged sites rather than being bound directly at a charged site as occurs with monovalent cation binding. This tendency would be greater the larger the size of the bound divalent cation. Thus, all the exchangeable Ba^{++} and Sr^{++} ions are so strongly associated with the surface, that the chloride exclusion area is zero. Thus, none of these exchangeable cations are free to develop ionic atmospheres in these systems. In other words, the diffuse layer is totally absent from these

TABLE 19

SURFACE AREAS OF DIVALENT CLAY MINERALS

Clay Mineral	Saturating Cation		Chloride Exclusion Area $m^2/g.$	Nitrogen Area $m^2/g.$
Fithian Illite				
	Mg^{++}		-7	
	Ca^{++}		16	102
	Sr^{++}		0	118
	Ba^{++}		0	
Wyoming Bentonite				
	Mg^{++}		74	59
	Ca^{++}		110	40
	Ba^{++}		64	47
Grundite Illite				
	Ca^{++}	(suspension)	102	94
		(powder)	69	
Milford Saponite				
	Ca^{++}		146	-

systems. However, the area of 16 m^2/g. obtained from chloride exclusion by Ca^{++} Fithian illite indicates that some of the exchangeable ions are dissociated, giving rise to double layer development over limited areas of surface.

The surface area of -7 m^2/g. obtained from the negative adsorption of chloride by Mg^{++} Fithian illite presumably arises through the tendency of the small doubly charged magnesium ion to hydrolyse at the surface. In this respect magnesium is behaving similarly to aluminium. In effect, positive charges are produced, which allow adsorption of chloride to occur. Since the general degree of ion association in the divalent Fithian illite systems is extremely high, it is not surprising that a nett positive adsorption of chloride is measured when the saturating cation is magnesium.

B. Chloride Exclusion by Wyoming Bentonite.

1. General Discussion.

Chloride exclusion results for Mg^{++}, Ca^{++} and Ba^{++} Wyoming bentonites are plotted in Fig. 26, according to Schofield's negative adsorption equation (39). The areas obtained from these measurements are compared with the nitrogen surface areas in Table 19.

Since all three systems possess a constant d(001) spacing of about 19 Å (Norrish, 1954) over the range of electrolyte concentrations used, no differences in chloride exclusion would be expected between the intra-crystalline regions of the three divalent ion systems. Thus the differences in chloride exclusion between Mg^{++}, Ca^{++} and Ba^{++} Wyoming

Chloride exclusion by divalent Wyoming bentonite systems.

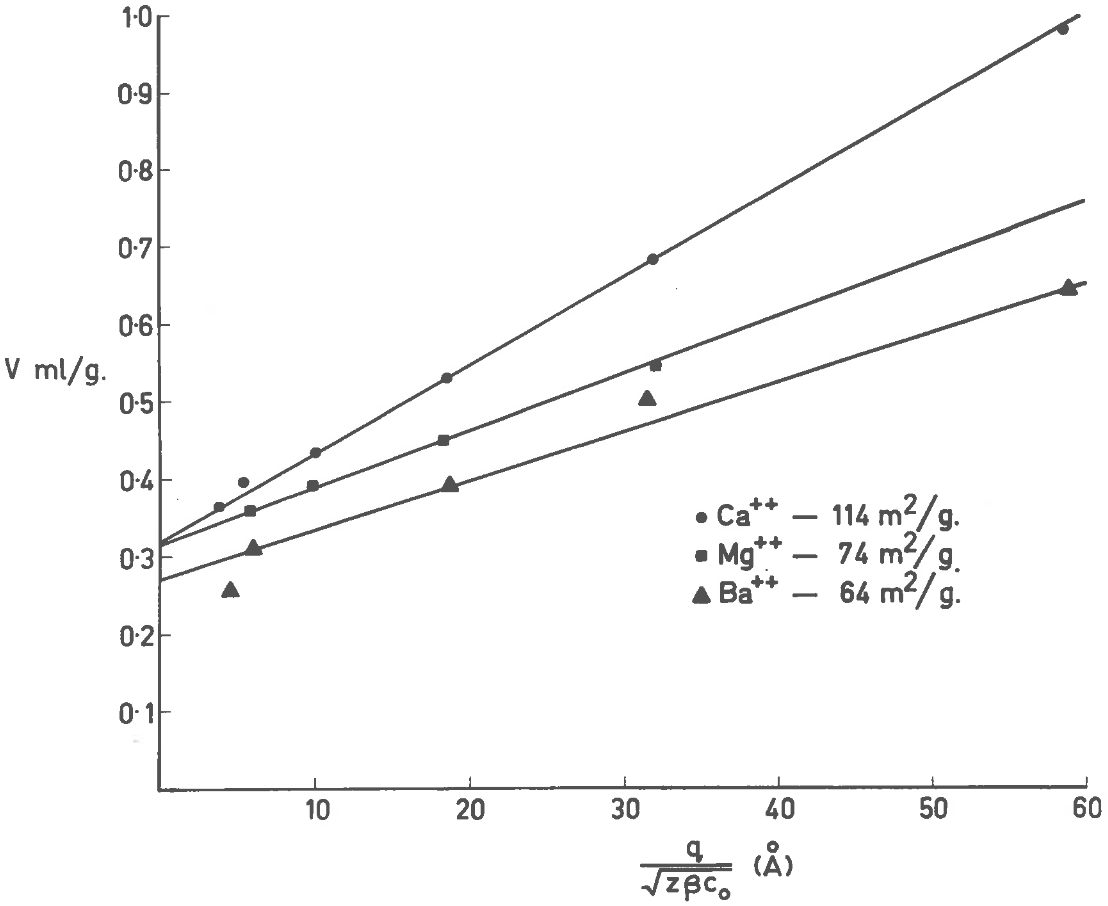


FIGURE 26.

bentonites may be explained in terms of differences in either binding on the external surfaces or differences in crystal size in suspension. The results for Ca^{++} Wyoming bentonite, to be discussed in detail below, may be explained in terms of exclusion from the intracrystalline region, together with complete exclusion from the external crystal surfaces, i.e. enough exchangeable ions are free to allow the full external surface area in suspension of 110 m^2/g. to be measured.

The results for Ba^{++} Wyoming bentonite are somewhat more difficult to interpret. The fact that the d(001) spacings of Ba^{++} and Ca^{++} Wyoming bentonite are much the same suggests that the crystal size in the two systems may be very similar (cf. Na^+ and Cs^+ Wyoming bentonites). If this is the case, not enough exchangeable Ba^{++} ions have dissociated from the external crystal surfaces to allow the full area to be measured. This appears probable since Ba^{++} is less hydrated and is therefore more likely to be associated with the surface.

Alternatively 64 m^2/g. may be the full area, in which case the difference between Ca^{++} and Ba^{++} Wyoming bentonites may be attributed to differences in crystal size in solution. Irrespective of the mechanism operating, it is not surprising that the nitrogen surface areas of Ca^{++} and Ba^{++} Wyoming bentonite are very similar. Thus, even if the difference in chloride exclusion is due to crystal size differences in suspension, drying and outgassing of the clays preceding the determination of the nitrogen surface areas would tend to enhance platelet association, particularly in the Ca^{++} system.

The nitrogen surface area of Mg^{++} Wyoming bentonite is also very much the same, whereas the chloride exclusion area is considerably less than would be expected from a comparison with the Ca^{++} and Ba^{++} results. The unexpectedly low area of Mg^{++} Wyoming bentonite may be attributed to positive adsorption of chloride by the free valency of the divalent ion, in the same manner as postulated for Mg^{++} Fithian illite. A hydrolysis mechanism, promoted by the association of the ion with a single site on the clay mineral surface may be involved. This would occur in much the same way as postulated by Jackson (1963) in discussing the hydrolysis of bound aluminium ions held at exchange sites. Jackson considered that chloride, sulphate and phosphate could substitute for hydroxyl in a reaction termed "anion penetration" by Bailar (1956). This process involves structural substitution through co-ordinate bonding, contrasting with an electrostatic anion exchange relationship analogous to simple cation exchange. The mechanism postulated is thus

$$-Mg^{++}(OH) + Cl^- \rightleftharpoons -Mg^{++}Cl + OH^-$$

Not all the exchangeable Mg^{++} ions would undergo hydrolysis; in fact the opportunity will only occur when the bound Mg^{++} ion possesses a free valency. Thus, substantial chloride exclusion still occurs in these Mg^{++} Wyoming bentonite systems, since positive adsorption of chloride under the experimental conditions (pH in the range 4-7) is not great enough to completely counteract chloride exclusion.

2. Detailed Interpretation of Calcium Wyoming Bentonite Results.

The results presented above for calcium Wyoming bentonite are very different from those reported by Bolt and Warkentin

(1956), and, in view of the fact that calcium montmorillonite has been demonstrated to have a 19 Å basal spacing for all $CaCl_2$ solutions less than molar (Norrish and Quirk, 1954), the high values obtained by Bolt and Warkentin probably arise through incomplete calcium saturation of the clay.

The surface density of charge of Wyoming bentonite (3.8×10^4 esu/cm^2) corresponds to a distance of separation of charges on the surfaces of 11.3 Å, which, together with an elementary silicate sheet separation of 9.4 Å approximates a uniform volume distribution of charge for the intra-crystalline regions. The simple Donnan theory for a 2:1 electrolyte was therefore applied to obtain the volumes of intra-crystalline water from which chloride was excluded. These values are given in Table 20.

The volume from which chloride was excluded by repulsion from external crystal surfaces (V_E) was obtained as the difference between the experimental value for chloride exclusion and the value calculated for the intra-crystalline regions. In Fig. 27, V_E is plotted against $\frac{q}{\sqrt{z\beta C_0}}$. The line drawn through the points for all concentrations cuts the abscissa at a value of 1.5 Å, indicating the virtual absence of any positive charges.

These results may further be compared with those of Edwards and Quirk (1962) in which the line drawn through all points for concentrations less than 10^{-2}M corresponded to a surface area of 85 m^2/g. In view of the results obtained by Quirk (1960) for kaolinite, it seemed reasonable to attribute deviations in the more concentrated solutions to

Chloride exclusion by calcium Wyoming bentonite suspensions in calcium chloride solutions of concentration c_o. The experimental results are shown together with calculated internal exclusion volumes when the Donnan theory for a 2:1 electrolyte is applied to the intracrystalline volume. The solid line for exclusion from external surfaces is obtained by subtracting the calculated internal exclusion from the total exclusion obtained experimentally.

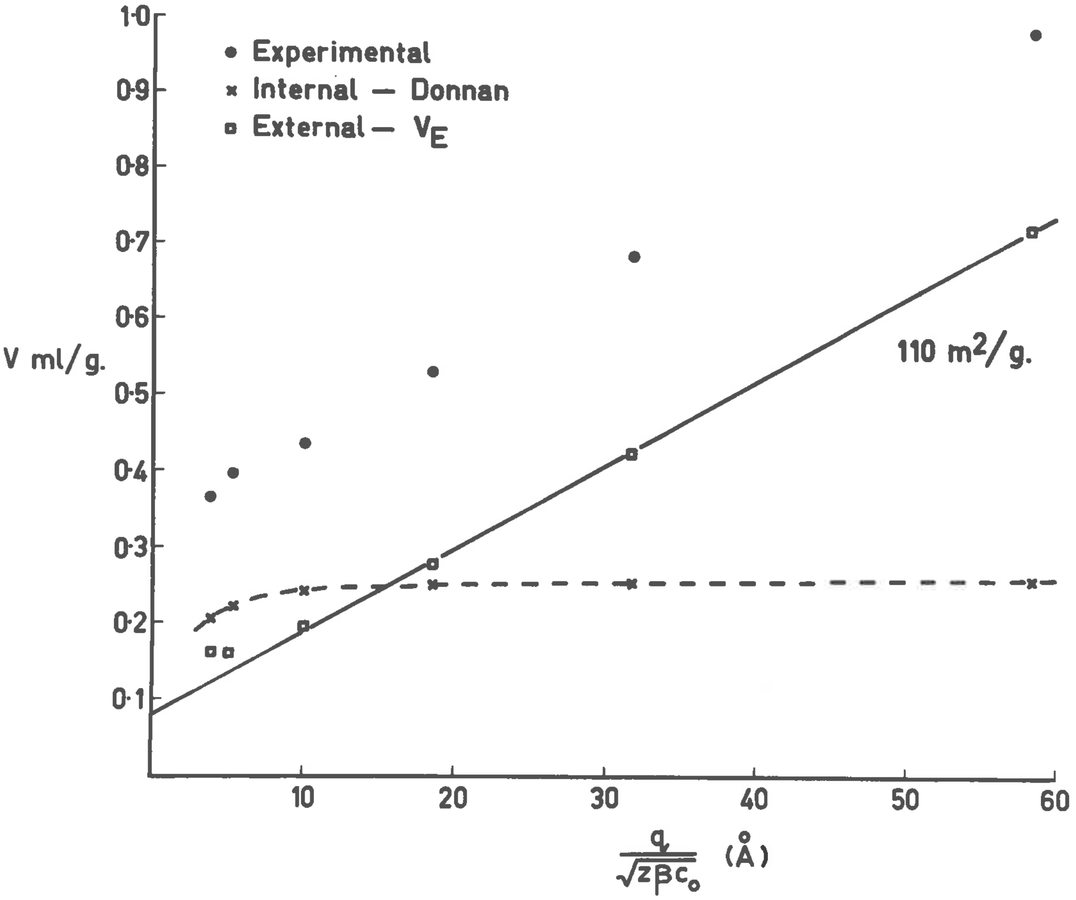


FIGURE 27.

TABLE 20

CHLORIDE EXCLUSION FROM EXTERNAL SURFACES OF CALCIUM WYOMING BENTONITE*

Molar concn. of $CaCl_2$	Calculated Donnan exclusion volume	Depth of exclusion on external surfaces	$\frac{\Gamma_-}{C_0}$
	ml/g.	Å	Å
0.25	0.212	6.2	4.5
0.15	0.225	7.0	5.8
0.05	0.241	11.5	10.0
0.015	0.252	22.5	18.3
0.005	0.257	41.0	31.7
0.0015	0.260	78.2	57.7

* See Fig. 27 for further details.

a concentration-dependent positive adsorption of chloride, promoted by hydrolysis of aluminium ions held at the exchange sites. The difference between the two sets of data lies in the method of clay preparation. Where an area of 110 m^2/g. was obtained the clay was prepared by way of the "standard state". Under these conditions exchangeable aluminium is kept to a minimum (Lin and Coleman, 1960), so that the possibility for positive adsorption of chloride occurring is also much reduced. The difference in area between the two calcium Wyoming bentonite systems may be attributed to slight differences in crystal size and ion association resulting from the method of preparation.

The dried calcium Wyoming bentonite used in these experiments gave a nitrogen surface area of 40 m^2/g. which is considerably less than the areas obtained with the suspensions. This is explained by the condensation of plates to give large crystals on drying, as proposed in discussing the monovalent Wyoming bentonite results. These ideas conform with those expressed by Blackmore and Warkentin (1960) and Aylmore and Quirk (1960 a, b).

C. Chloride Exclusion by Grundite Illite.

Chloride exclusion measurements were conducted on both the suspension and powder of Ca^{++} Grundite illite, in equilibrium with a range of electrolyte concentrations. The results are presented in Fig. 28. The suspension gave an area of 102 m^2/g., while the area obtained from measurements on the oven-dried (70°C) powder was only 69 m^2/g. These areas may further be compared with the area of 94 m^2/g. obtained

Chloride exclusion by calcium Grundite illite.

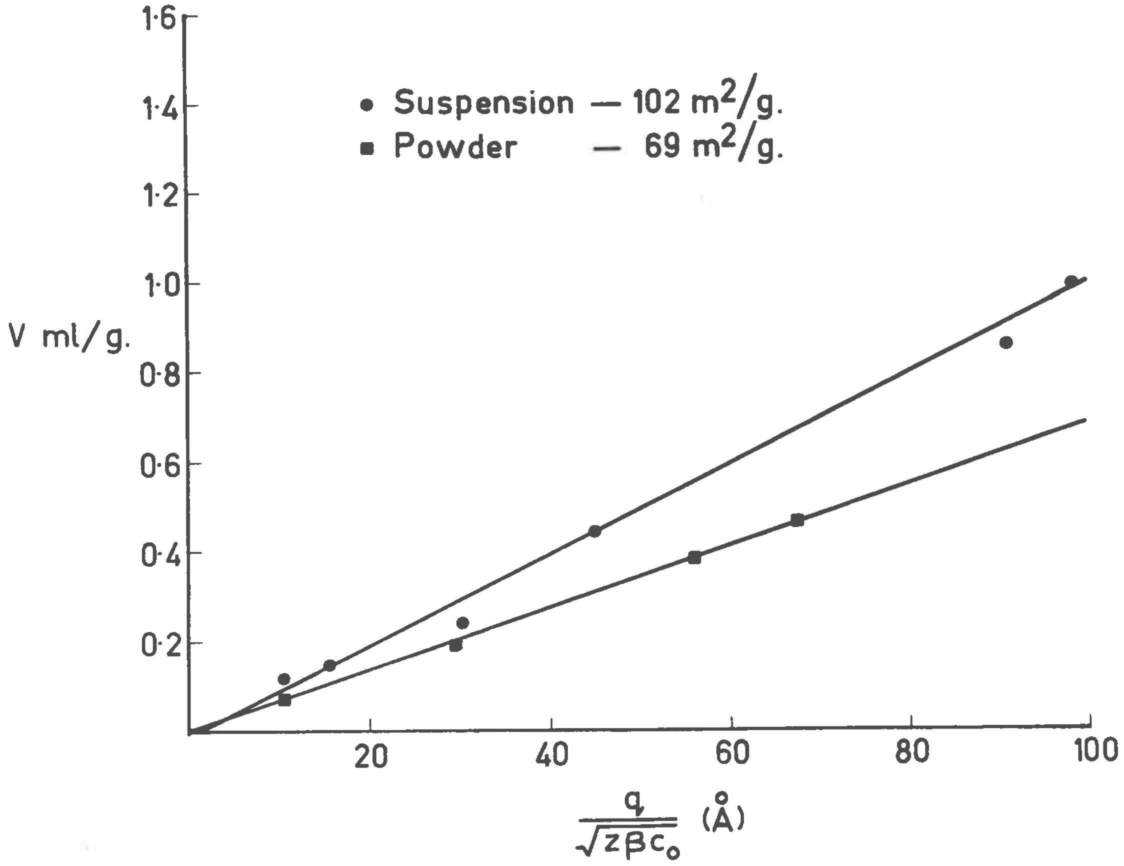


FIGURE 28

from low temperature nitrogen adsorption.

Although Grundite illite is interstratified to some extent, the chloride exclusion results indicate that enough exchangeable Ca^{++} ions dissociate from the external crystal surfaces in the suspension phase to allow the full area to be measured. A basal d(001) spacing of about 19 Å or less would be expected in the interstratified regions. However, in the powder phase, the results indicate that not enough exchangeable ions dissociate to allow the full surface area to be measured. This may occur because the drying process enhances binding or a structure may be formed which limits, to a certain extent, double layer development.

The comparatively large exclusion volumes compared with those obtained for Ca^{++} Fithian illite suggest the possibility that the external surfaces of the interstratified illites may be more like montmorillonite than mica surfaces.

The agreement between the nitrogen and the dispersion surface areas indicates that the crystal size is not changed on out-gassing. There are thus no grounds for attributing the lower surface area of the powder phase to an increase in crystal size.

D. Chloride Exclusion by Milford Saponite.

Chloride exclusion results for Ca^{++} Milford saponite (Fig. 29) are very similar to those reported above for Ca^{++} Wyoming bentonite. The most noticeable features of the Schofield plot are the intercept of 0.35 ml/g. and the surface area of 146 m^2/g. obtained from the slope

Chloride exclusion by calcium Milford saponite.

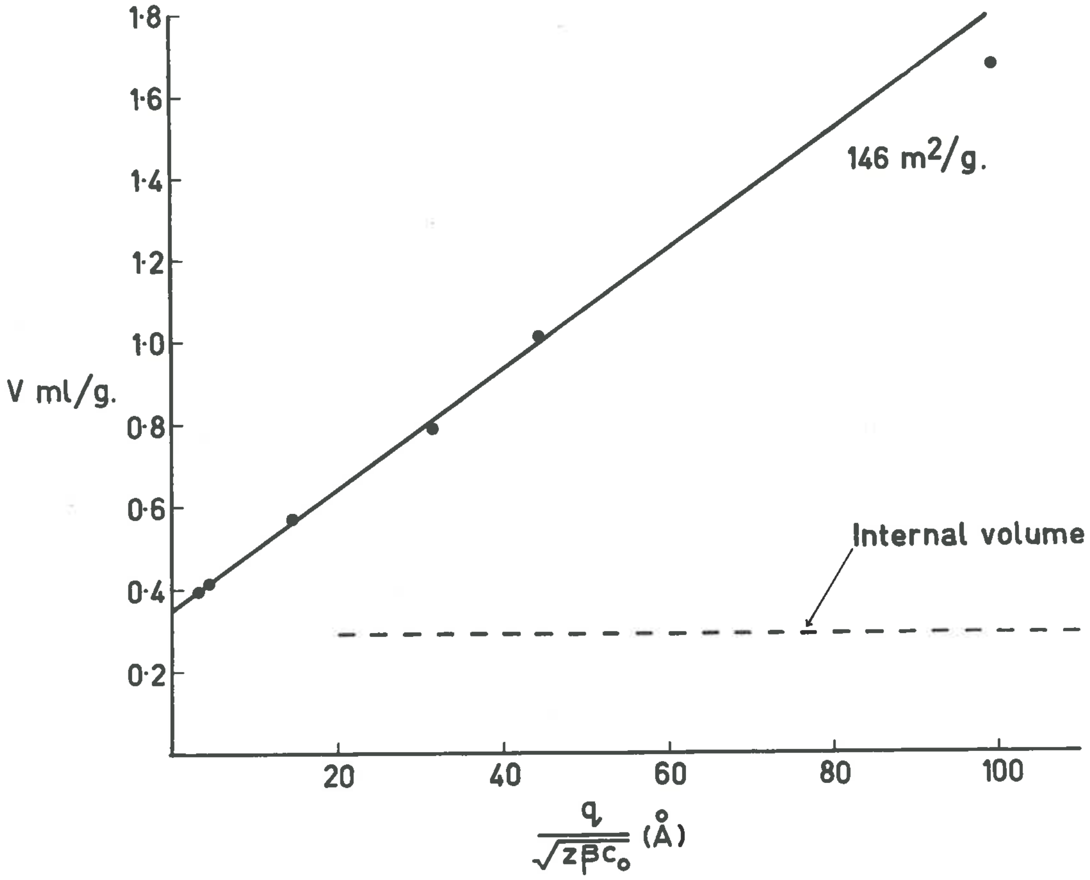


FIGURE 29

of the line.

Calcium saponite showed very similar X-ray diffraction behaviour to calcium montmorillonite in that it gave a rational series of orders of d(001) = 18.7 Å. The chloride exclusion results can thus be interpreted in terms of exclusion from the intra-crystalline regions coupled with free double layer development on external crystal surfaces, i.e. enough free ions are present in the diffuse layer to allow the full area to be measured. The analysis of the system in these terms is shown in Table 21. It may be seen that there is good agreement between the experimentally determined and the expected depths of exclusion on external surfaces, particularly at low electrolyte concentrations. However, at higher concentrations considerable discrepancies occur. The reasons for these deviations are not at all clear. A crystal size effect could be involved, but the results for the montmorillonite systems indicate that this is not the reason. The deviations cannot be attributed to the charge density of Milford saponite (4.7×10^4 esu/cm^2). However, since a considerable proportion of the charge arises from substitution in the tetrahedral layer, this may lead to more extensive ion binding at higher concentrations. This behaviour is somewhat similar to caesium Grundite illite, for which complete ion association occurs at concentrations greater than 0.1 N.

III. TRIVALENT ALUMINIUM SYSTEMS.

Chloride adsorption data obtained for both aluminium saturated Fithian illite and Wyoming bentonite showed that predominantly nett positive adsorption occurred in these systems, although a nett negative

TABLE 21

CHLORIDE EXCLUSION FROM EXTERNAL SURFACES OF CALCIUM SAPONITE

Molar concn. of $CaCl_2$	Total vol. of exclusion	External vol. of exclusion	Depth of exclusion on external surfaces	$\frac{\Gamma^-}{C_o}$
	ml/g.	ml/g.	Å	Å
0.497	0.394	0.103	7.0	0.8
0.248	0.418	0.127	8.5	2.1
0.0245	0.582	0.291	19.9	11.9
0.0050	0.789	0.498	34.1	29.0
0.0025	1.024	0.733	50.2	42.0
0.0005	1.672	1.381	94.6	98.4

adsorption may be obtained at high electrolyte concentrations. The results are calculated and plotted according to Schofield's negative adsorption equation in Fig. 30. It may be seen that sensible surface areas of the two clay minerals cannot be obtained from these plots.

The results indicate that the amount of positive adsorption of chloride by aluminium Fithian illite is greater, than that by aluminium Wyoming bentonite at the same concentration. This may be attributed to the greater charge density of the Fithian illite together with the fact that aluminium ions in the interlamellar regions of Wyoming bentonite are less prone to hydrolysis. It is postulated that before an aluminium ion can positively adsorb chloride ions it must be bound to the clay mineral surface. Then positive adsorption of chloride occurs as a result of hydrolysis and replacement thus :-

$$-\mathrm{Al}-\mathrm{OH} + \mathrm{H}^+ + \mathrm{Cl}^- \rightleftharpoons -\mathrm{AlOH}_2^+ - \mathrm{Cl}^-$$

It is further considered that the amount of positive adsorption of chloride will bear a rather direct relationship to the amount of aluminium bound at the clay mineral surface. Thus aluminium would seem to be bound completely on the external surfaces of Fithian illite. However, every bound aluminium ion is not associated with three charged sites arising from isomorphous substitution in the clay mineral lattice. The unsatisfied aluminium valencies are able to positively adsorb chloride.

A very similar situation will undoubtedly prevail in the Al^{+++} Wyoming bentonite system, with virtually all exchangeable ions, both

Chloride exclusion by aluminium clay suspensions.

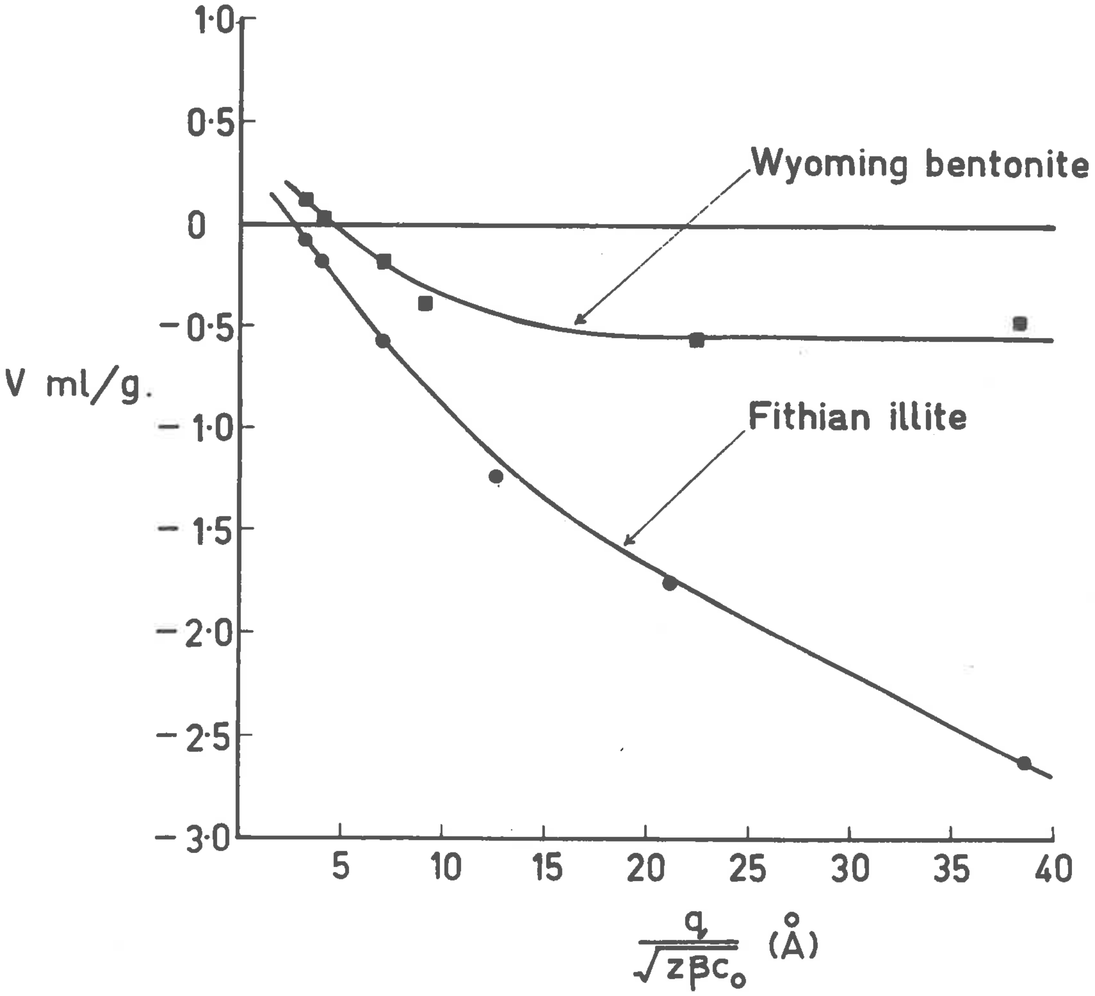


FIGURE 30.

interlayer and external associated with the clay surface. Once again, positive adsorption occurs because of hydrolysis of bound aluminium ions, particularly on the external crystal surfaces.

IV. CONTROLLED pH EXPERIMENTS.

In view of the previous discussion of the results to be expected for surfaces of varying charge density, it seems extremely unlikely that any significant differences in chloride exclusion associated with the development of extra negative charges at high pH would be obtained. However, the model based on discrete charged sites would allow for increases in chloride repulsion with an increase in negative charge. For instance, if there were ten associated sites and ten dissociated sites, and another negative site arose as follows,

$$-\mathrm{SiOH} \rightleftharpoons -\mathrm{SiO}^- + \mathrm{H}^+$$

this could contribute to the negative adsorption unless a cation becomes associated with the new site immediately. However, the presence of positive charges in these systems could have a much more pronounced effect.

The effect of pH on chloride exclusion by Na^+ and Ca^{++} Grundite illite and Ca^{++} Wyoming bentonite is shown in Figs. 31-33. The measured volumes of chloride exclusion have been plotted against the equilibrium pH. Without exception, the plots indicate that chloride exclusion from a given electrolyte concentration is independent of pH

Effect of pH on chloride exclusion by sodium Grundite illite suspensions in NaCl.

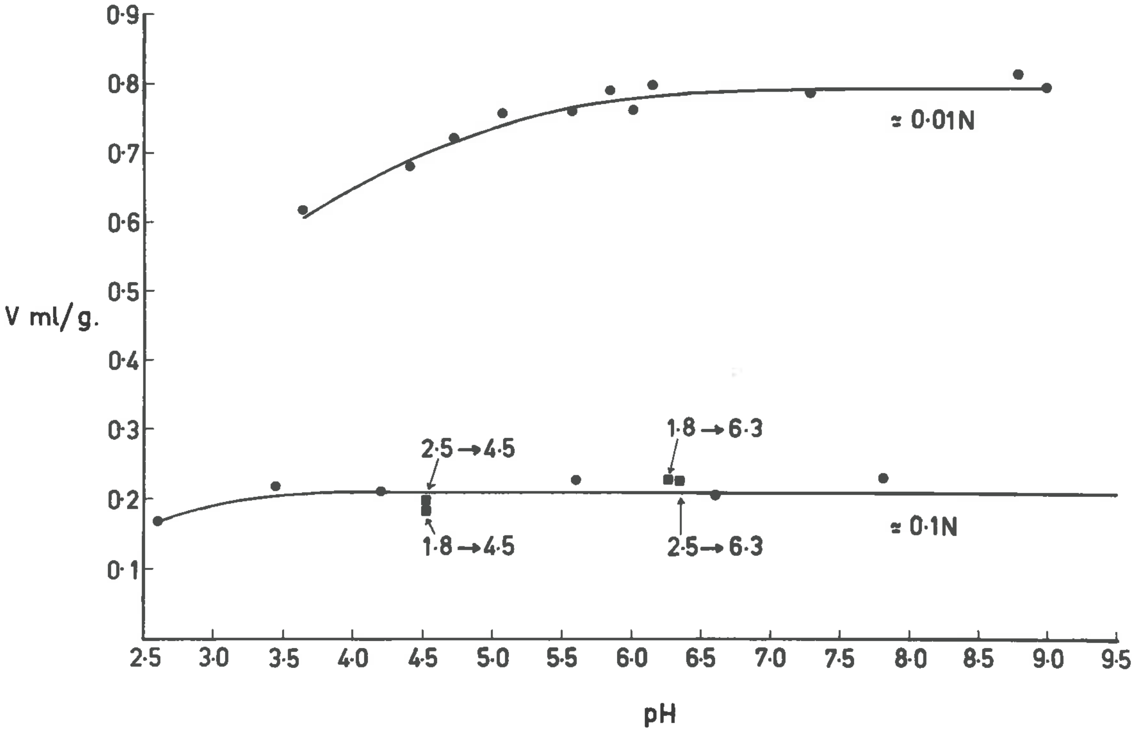


FIGURE 31.

Effect of pH on chloride exclusion by calcium Grundite illite suspensions in approximately 0·05M $CaCl_2$ solutions.

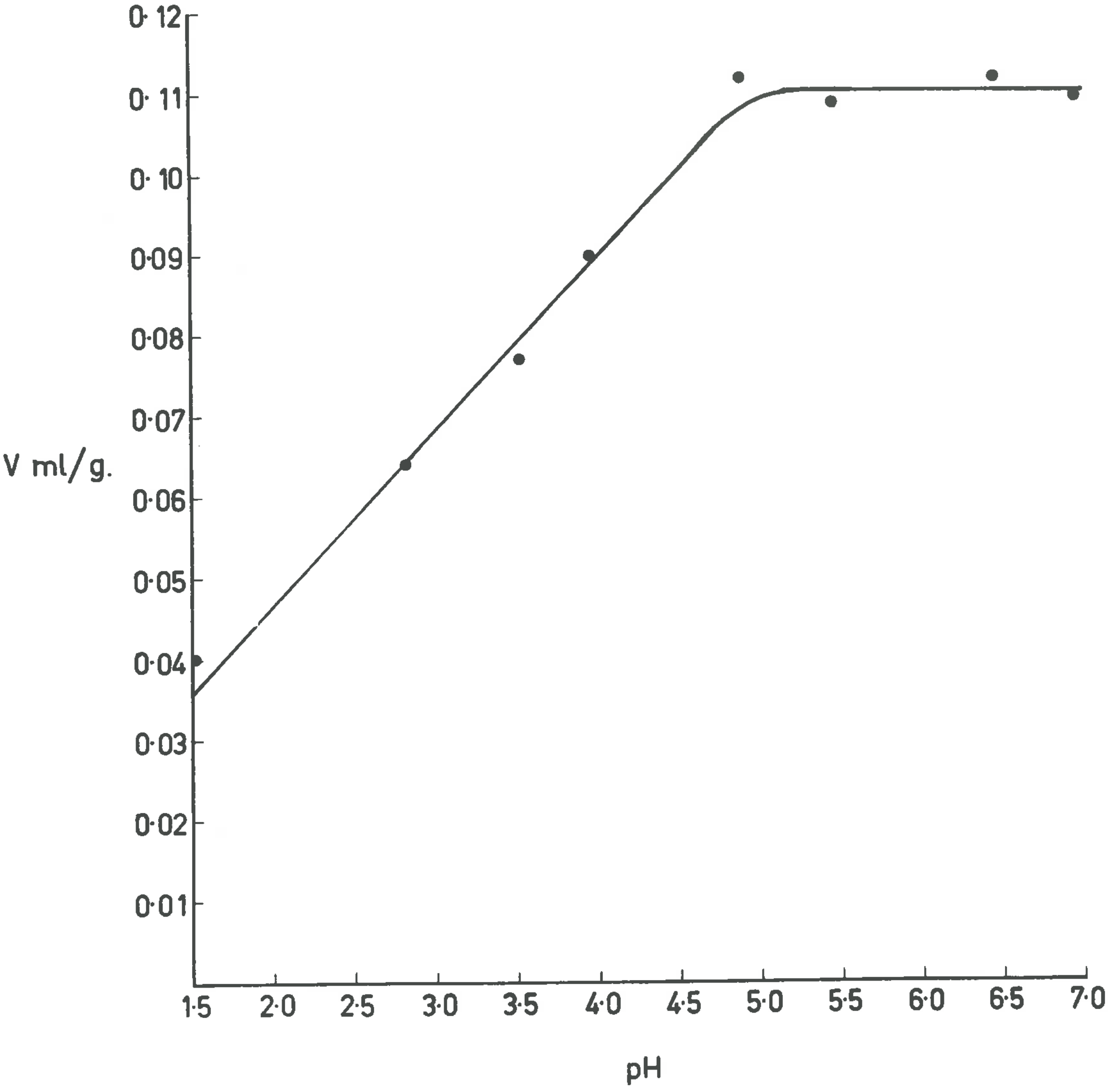


FIGURE 32.

Effect of pH on chloride exclusion by calcium Wyoming bentonite.

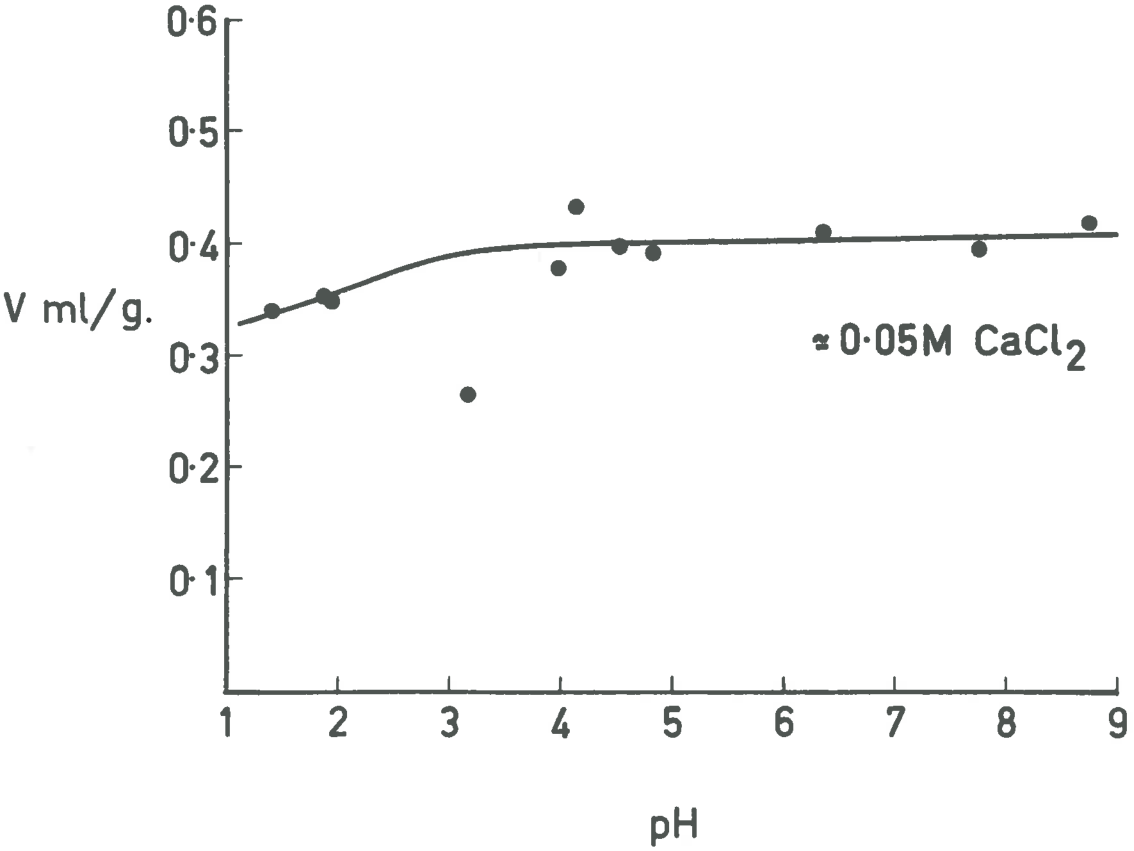


FIGURE 33.

over the range 4.0 - 9.0. However, at lower values of pH there is a slight suggestion that positive charges are present in all systems. Most probably, they arise from hydrolysis of the small amounts of exchangeable aluminium ions that remain as traces after the standard preparation procedure. There is no evidence that the slight decrease in chloride exclusion at low pH values is due to a decrease in negative charge, since the pK of $-SiO^-H^+$ is about pH 9. The negative charge is permanent, arising from isomorphous replacement within the crystal lattice of the clay mineral. Thus, in agreement with Schofield (1949) it is considered that changes in nett charge carried by clay minerals at low pH is due to the development of positive charges only.

The relative constancy of the chloride exclusion data for a particular electrolyte concentration over the pH range 4.0 - 9.0, is not in conflict with the conclusions of Schofield (1949) that there is an increase in negative charge at high pH values. These sites, which Schofield considered were uncharged at pH values less than 6.0, become negatively charged by the following mechanism

$$-SiOH \rightleftharpoons -Si{-}O^- + H^+$$

Nevertheless, some extremely interesting results were obtained at high pH values for the Na^+ Grundite illite system. The expected pH values for the addition of known amounts of NaOH were obtained from the titration curve of the Na^+ Grundite illite suspension in 0.011 N NaCl. After equilibration for three days, the final values of pH were measured, and shown to be substantially less than expected. This consumption of NaOH may be used as a criterion for the development of extra negative charges at high pH. These calculations presented in Table 22, indicate that up to 20 per cent extra negative charge was developed in these systems. However, as shown in Fig. 31, the extra negative charge did not result in any increase in chloride exclusion. On the other hand, at the highest pH value (12.4) there was a reduction in chloride exclusion to about one-half that measured over the pH range 4-11. This reduction is due to the simultaneous exclusion of chloride from 0.011 N NaCl and hydroxyl ions from a concentration of much the same order. ($\simeq$ 0.028 N). At all other pH values the hydroxyl ion concentration is so relatively low that it is not able to effectively compete with chloride. Hence, the chloride repulsion does not change with pH.

The amount of positive charge developed in these systems was shown to be pH dependent. Chloride exclusion measurements on sodium Grundite illite suspensions which were equilibrated at low pH (1.8, 2.5) and then adjusted to high pH (4.5, 6.25) showed no differences from systems equilibrated at high pH. This suggests that the amount of positive charge developed is reversible providing that there is no lattice breakdown. Quirk (1960) obtained a similar pH effect on the positive adsorption of chloride by the edge face of Rocky Gully kaolinite crystals.

V. CHLORIDE EXCLUSION BY SILICA.

Chloride exclusion measurements were conducted on an amorphous

TABLE 22

DEVELOPMENT OF EXTRA NEGATIVE CHARGE AT HIGH pH IN SODIUM GRUNDITE ILLITE SUSPENSIONS IN 0.011 N NaCl

Expected final pH	Measured final pH	Consumption of OH^- meq/g. clay	Nett negative* charge meq/g.
12.26	12.44	-	-
11.61	10.68	0.045	0.348
11.37	8.77	0.031	0.334
11.26	7.28	0.024	0.327
11.00	6.39	0.013	0.316

* Exchange capacity = 0.303 meq./g.

silica powder possessing a nitrogen surface area of 155 m^2/g. The experimental results of exclusion from sodium and caesium chloride solutions under a range of different concentrations and pH conditions are presented in Figs. 34 and 35 respectively.

The Schofield plot of the sodium chloride results indicates that there is a very marked dependence of surface area on pH (Table 23). However, in interpreting these results, care must be taken in distinguishing between exclusion due to the development of extra negative charges at high pH and purely mechanical exclusion from the small pores associated with uncharged silica surfaces, as discussed by Dalton, McClanahan and Maatman (1962). These authors showed that mechanical exclusion was pH independent. Thus, since these results show a marked pH dependence, the results must be interpreted in terms of an increase in the number of negative charges with increasing pH. The structural factor is still responsible however, for the volume intercept of 0.10 ml/g. obtained for all systems.

In considering the exclusion results from NaCl solutions in terms of changes in charge density, Bolt's (1957) results for the charge density of "Ludox" colloidal silica particles have been transposed into units of esu/cm^2, and are presented as such in Table 24. Although not directly applicable to the material used here, Bolt's figures show the general trend to be expected from the effects of pH and electrolyte concentration on charge density. At low values of pH, the low charge on the surface causes a reduction in surface area. As the pH is increased, more hydroxyl groups dissociate giving rise to a greater charge, resulting in greater exclusion volumes and larger surface areas.

Chloride exclusion by silica powder from NaCl.

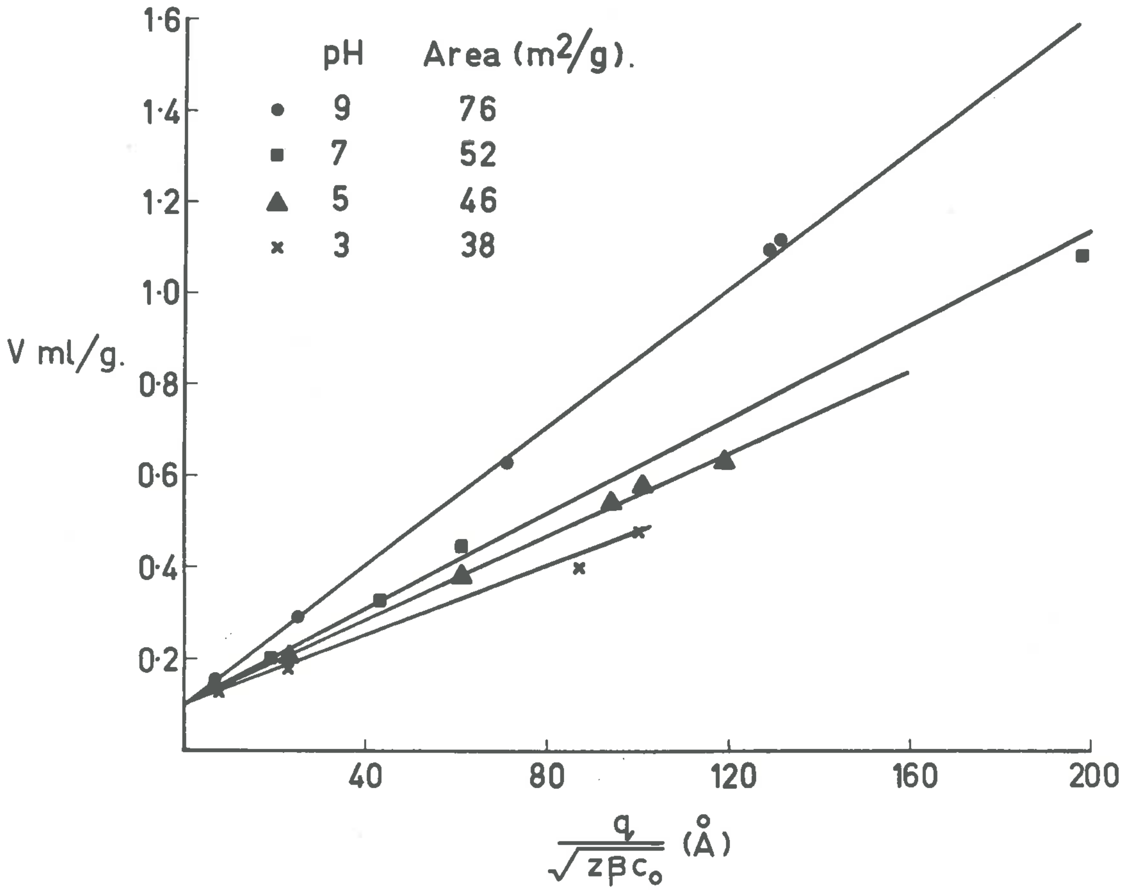


FIGURE 34.

Chloride exclusion by silica powder from CsCl.

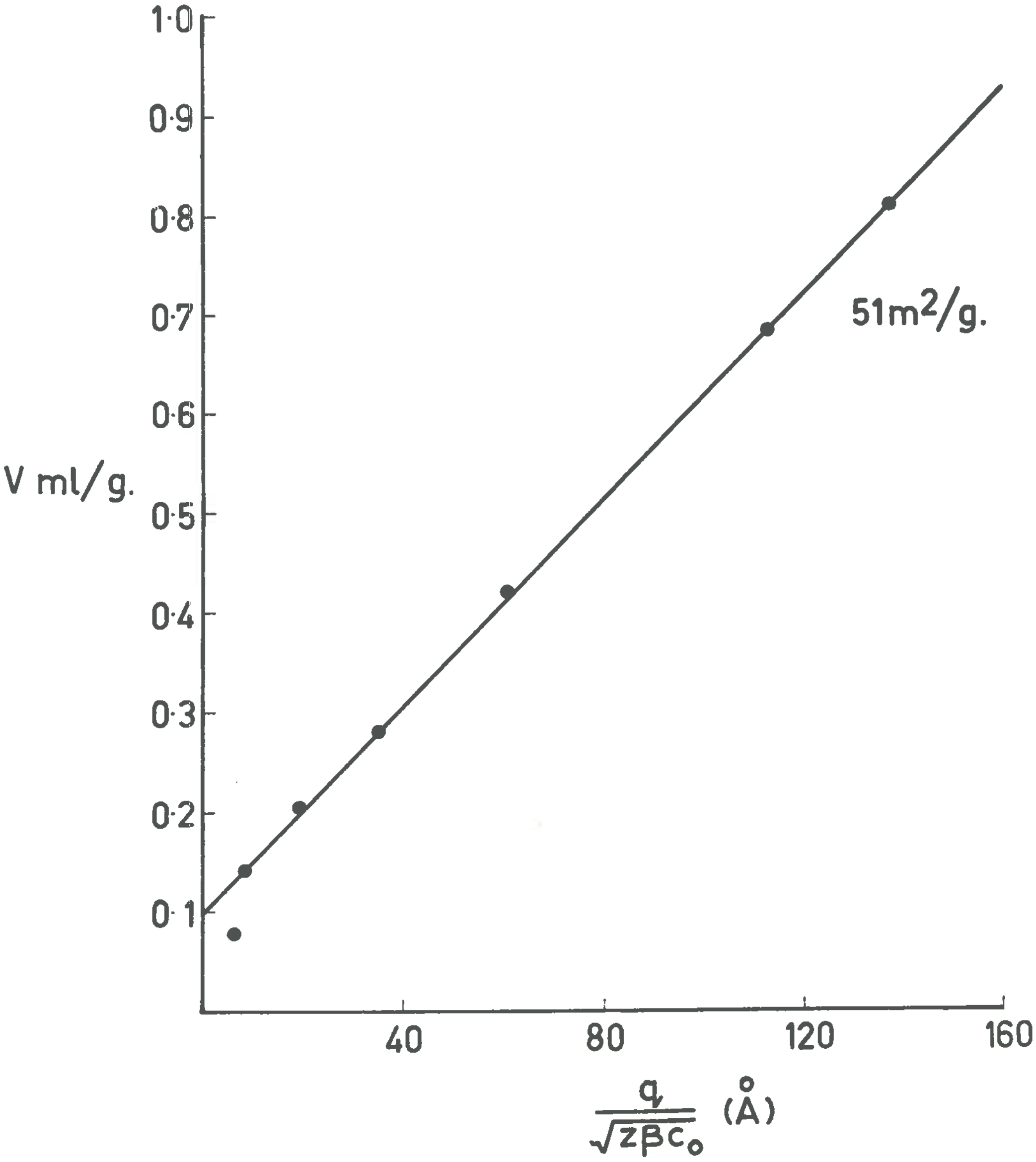


FIGURE 35.

TABLE 23

EFFECT OF pH ON CHLORIDE EXCLUSION AREA OF SILICA

	pH	Area (m^2/g.)
NaCl	3	38
	5	46
	7	52
	9	76
CsCl		51

TABLE 24

SURFACE DENSITY OF CHARGE (σ) OF "LUDOX" COLLOIDAL SILICA PARTICLES AS A FUNCTION OF ELECTROLYTE CONCENTRATION AND pH

pH	0.001 N	0.01 N	0.1 N
5	0.06×10^4	0.09×10^4	0.18×10^4
6	0.15×10^4	0.27×10^4	0.45×10^4
7	0.31×10^4	0.54×10^4	0.96×10^4
8	0.66×10^4	1.14×10^4	1.86×10^4
9	1.35×10^4	2.07×10^4	3.48×10^4
10	2.55×10^4	3.84×10^4	5.94×10^4

Calculated chloride exclusion volumes from the charge density values of Bolt's (1957) colloidal silica suggest that the higher the pH, the more nearly the chloride exclusion area approaches the nitrogen surface area. However, the maximum surface area reported here of 76 m^2/g. does not even approach the nitrogen area of 155 m^2/g. A possible reason for this discrepancy, may be that the silica powder used in this work has a much lower charge density than that of Bolt's "Ludox" colloidal silica under the same conditions.

One of the interesting features of the results is that straight lines are obtained at all pH values. This observation conforms with the discrete site model discussed earlier. In this model an increase in $(^2/K)^2$ is compensated by an increase in ion association, i.e. the number of associated sites is directly proportional to the concentration.

The surface area obtained from chloride exclusion by silica from CsCl at uncontrolled pH was 51 m^2/g. The pH in these systems would have been in the range 6.0 - 8.0. The close similarity between these results and the chloride exclusion from NaCl at pH 7, indicates that exactly the same mechanism is operating in both systems. There is no preferential binding of caesium ions as occurs in the clay mineral systems. The charge in the silica systems is quite variable, merely arising from the dissociation of surface OH^- groups, which is both concentration and pH dependent. Furthermore, the charge in these systems may be as much as two orders of magnitude less than the permanent isomorphous replacement charge of the clay minerals. This has been confirmed by both O'Connor and Buchanan (1956) and Bolt (1957).

4. GENERAL DISCUSSION.

The repulsion of negative ions from a negatively charged surface has been considered by Schofield (1947, 1949) who on the assumption of a smeared out charge derived the following equation:-

$$\frac{\Gamma_-}{C_0} = \frac{q}{\sqrt{z\beta C_0}} - \frac{4}{z\beta\Gamma}$$

This equation is applicable when the first term greatly exceeds the second term, i.e. when the surface density of charge on the interface is high. A more complete treatment of the phenomenon of ion exclusion has been given by Overbeek (1956).

It was considered that the most appropriate way of testing the above equation was to compare the surface area measured by low temperature nitrogen adsorption with that obtained from chloride repulsion measurements. This comparison would have to be made for a system where it would be expected that the area available for water and nitrogen adsorption would be virtually identical. This has been done to a limited extent by some workers, and from their measurements it would appear that the equation is more or less satisfactory. It was therefore considered appropriate that more extensive and detailed measurements of chloride exclusion from negatively charged surfaces should be obtained.

To meet the requirement that the area available for nitrogen (at -195°C) and water was essentially similar, very critical measurements were made on Fithian illite, a non-expanding, mica-like material for which no evidence of interstratification was found.

The exclusion of chloride from samples of this clay was determined using an electrometric titration method coupled with weighings of the supernatant liquid and the clay plus entrained solution. The results were expressed as a volume of water from which chloride was completely excluded by the clay surface. According to Schofield, when this volume (i.e. $\frac{\Gamma_-}{C_0}.A$ where A is the surface area) is plotted against $\frac{q}{\sqrt{z\beta C_0}}$, the slope of the straight line plot obtained should provide the area of the charged interface.

When the repulsion of chloride by Fithian illite saturated with a series of alkali metal cations was studied, it was found that the area derived from the experimental measurements ranged from 80 m^2/g. for the Li-system to zero for the Cs-system (see Fig. 9). The nitrogen surface areas of the various homoionic Fithian illites were all about 110 m^2/g.

The most interesting feature of these results is that for all the monovalent ion systems a straight line is obtained when the exclusion volume $\frac{\Gamma_-}{C_0}.A$ is plotted against $\frac{q}{\sqrt{z\beta C_0}}$. These straight line plots exclude one possible explanation of the results, viz. that the surface density of charge has been lowered by ion association with the surface. However, for a surface density of charge low enough to cause deviations from Schofield's equation, curved plots should be obtained if the assumption of a smeared out charge is met.

An alternative explanation of the results presented in Fig. 9, is that the charge can no longer be regarded as being smeared out over the whole surface. The results have been satisfactorily analysed in terms of independent sites of localized charge. The areas from which ions are dissociated are those which will cause chloride exclusion. Each individual dissociated site would be expected to follow the Schofield equation for a monovalent ion, because $\frac{q}{\sqrt{z\beta C_0}}$ is identical with $\frac{2}{K}$, i.e. the exclusion is the same as that for a single ion. On those parts of the surface where an ion is bound, chloride exclusion will not be measured, and hence when ion binding occurs, the total surface area of the charged interface will be underestimated.

The distribution of bound ions in the adsorbed layer immediately adjacent to the charged surface was considered in terms of ions bound immediately at the surface and ions that are bound one water molecule away from the surface. It is considered that ions bound at the immediate surface form "Fuoss-type" ion pairs in the Inner Helmholtz Plane, while those bound in the Outer Helmholtz plane one water layer removed from the charged surface form "Bjerrum-type" ion pairs. Neither type of bound ion can be involved in diffuse layer formation because the electrostatic forces holding the ions are so large compared to kT, that the counterions do not have the mobility which permits them to move out of the adsorbed layer. Thus, association and dissociation may be partly considered as a matter of relative mobility. The association in terms of ion pair formation is very different from association in the sense originally defined by Arrhenius (1887). Furthermore, ion binding (immobilization) results from a large number of charges on a fixed surface; the number of bound counterions increases with decreasing electrolyte concentration, because of the increase in magnitude of the electrostatic forces involved.

To equate the various forces acting in the adsorbed region it was necessary to define a reference electrolyte concentration, which was taken as the concentration at which the area of the ionic atmosphere is equal to the area of surface associated with each charge. If no ion binding occurred, an area of about 110 m^2/g. would have been measured for all the Fithian illite systems. The amount by which A is less than this gives a measure of ion binding. The binding energy per unit weight of clay which was defined as the difference between the free energy of diffuse double layer formation on the external area of 110 m^2/g. and the measured area A, at the reference concentration was equated to the nett electrostatic energy between a cation and the negatively charged illite surface. This nett energy was considered to arise from ion attraction between the oppositely charged ion and surface site, and repulsion due to image forces which arises because the dielectric constant of the surface region is lower than that of the bulk solution. The final derived equation is

$$r\theta = \frac{-(\varepsilon_w - \varepsilon_m) K \sigma z e}{\varepsilon_w(\varepsilon_w + \varepsilon_m) 16 n k T \left(\cosh \frac{z e \psi_0}{2kT} - 1\right)} + \frac{z e \sigma (\varepsilon_m - \varepsilon_w) K p}{\varepsilon_w \cdot \varepsilon_m \cdot 8 n k T \left(\cosh \frac{z e \psi_0}{2kT} - 1\right)}$$

$$+ \frac{\pi \sigma^2 K r^2}{(\varepsilon_w + \varepsilon_m) 4 n k T \left(\cosh \frac{z e \psi_0}{2kT} - 1\right)}$$

All symbols have been defined earlier. The second term on the right hand side is a term for the re-arrangement of water molecules when ion binding occurs and is based on the Born hydration energy concept. The chloride exclusion results were plotted according to this derived equation using the hydrated ion radius (Fig. 16). Good agreement between theory and experimental results was obtained. This supports the proposed model of ion binding at discrete charged sites in a similar manner to the site binding hypothesis for polyelectrolyte systems, in which the counterions are localized on or near charged sites by the high electrostatic potential originating in the fixed charges.

The chloride exclusion results for the divalent Fithian illite systems indicate that the amount of ion binding on the high charge density surfaces is very large, even when the saturating cation is calcium. The trivalent aluminium system is characterized by a concentration dependent positive adsorption of chloride, a feature which also arises in the magnesium system to a limited extent.

The chloride exclusion results from the lower charge density, expanding lattice Wyoming bentonite saturated with monovalent cations were also plotted according to Schofield's equation. The areas obtained ranged from 625 m^2/g. for the Li-system to 156 m^2/g. for the Cs-system. These areas were all less than the theoretical area of about 700 m^2/g. calculable from crystallographic data, because the clay plates persist in crystals. The nitrogen surface areas of the homo-ionic Wyoming bentonites were generally about 60 m^2/g. except caesium Wyoming bentonite which had an area of 146 m^2/g. The agreement between the nitrogen and chloride exclusion areas for caesium Wyoming bentonite suggests that these large uniform crystals tend to behave as separate entities. However, in the other systems drying cause further condensation of small mobile platelets which is not possible with caesium.

The general ion binding theory was applied to the Wyoming bentonite results and shown to be more applicable to the Li- and Na- and to a lesser extent K- systems than the NH_4^- and Cs- systems. In the former systems, diffuse double layers form between opposed plates within a crystal as well as on the external crystal surfaces. In the latter systems, there is a strongly increasing tendency for the plates within a crystal to be separated by only one or two water layers. It is believed that the presence of a small mobile montmorillonite plate promotes through a co-operative energy mechanism an increased association of the larger, less hydrated ions for the surface.

The agreement between the nitrogen adsorption and chloride exclusion areas of caesium Wyoming bentonite further suggests that enough exchangeable ions have dissociated from the external surface to allow the total external area to be measured. The detailed analysis of the sodium Wyoming bentonite results also suggests that enough sodium ions have dissociated and developed ionic atmospheres to allow the total external area to be measured. In the higher charge density Fithian illite systems, not enough exchangeable cations ever dissociate to allow the full external area to be measured.

The total theoretical area of 700 m^2/g. is never measured because the platelets persist in crystals, even at very low electrolyte concentrations. The reductions in area below 700 m^2/g. may be attributed to the interaction of diffuse double layers or to the inability of the repulsive forces to overcome the attractive potential barrier in those systems where a fixed spacing occurs. Irrespective of the saturating cation, enough ions dissociate from the external crystal surfaces to allow the full external surface area to be measured. Schofield's equation will always hold for the external crystal surfaces of Wyoming bentonite.

The results for the divalent Wyoming bentonite systems were likewise interpreted in terms of a fixed spacing between plates within a crystal coupled with exclusion from external surfaces. The external surface area of the Ca- system was greater than that of the Ba- system, probably because more exchangeable ions were dissociated from the external crystal surfaces. However, an alternative explanation was also possible, based on differences in crystal size in suspension. The magnesium Wyoming bentonite results were anomalous, and led to the suggestion that hydrolysis mechanism may be involved, which leads to the creation of positive adsorption sites. The trivalent aluminium Wyoming bentonite systems were characterized by a nett positive adsorption of chloride at all electrolyte concentrations. A hydrolysis mechanism is considered to be operative.

The limited crystalline swelling of montmorillonite and expanding lattice minerals can be regarded as an effect of ion association.

The chloride exclusion results for sodium and caesium Grundite illite and Milford saponite systems were also analysed using the general ion binding theory. Grundite illite is an interstratified material showing characteristics of both the Fithian illite and Wyoming bentonite systems. Milford saponite is an expanding-lattice mineral possessing a nett negative charge which is tetrahedral in origin.

The results for the interstratified Grundite illite systems indicate that incomplete exclusion occurs from the external surfaces, because not enough ions are dissociated. In the Na- system, the full suspension area of 161m^2/g. (Greenland and Quirk, 1962) is not measured because of double layer interaction coupled with incomplete external exclusion. However, chloride exclusion from calcium Grundite illite suspensions indicated that the full external area may be measured. This suggests that the external surfaces of the interstratified illites may be more like montmorillonite than mica surfaces.

The Milford saponite results were extremely interesting, particularly in comparison with the other systems. Sodium Milford saponite gave a chloride exclusion area of 740 m^2/g., while that of the Cs-system was only 66 m^2/g. The nitrogen surface areas were 9.4 m^2/g. and 152 m^2/g. respectively. These results may now be compared with those for Wyoming bentonite and Fithian illite in terms of the density of charge and the site of origin of the charge.

The charge density of Milford saponite (4.7 x 10^4 esu/cm^2) lies between that of Wyoming bentonite (3.3 x 10^4 esu/cm^2) and Fithian illite (8.2 x 10^4 esu/cm^2). The behaviour of Na saponite and montmorillonite is very similar, the full external area being measured. The full external area of Fithian illite is not measured for any saturating cation. The caesium results show a similar trend; the full external area of the montmorillonite is measured, while zero area is measured in the Fithian illite system. The Cs- saponite system is intermediate.

The charge on the surfaces of the non-expanding Fithian illite and the expanding lattice Milford saponite systems arises from isomorphous substitution in the tetrahedral layer, whereas the permanent charge carried by Wyoming bentonite originates in the octahedral layer. If the site of origin of the charge was significant in the ion binding phenomenon, it would be expected that a given cation would be bound more strongly on a surface where the charge arises tetrahedrally rather than on one where the charge is octahedral in origin. Thus, for instance, ion binding on the external surfaces of Milford saponite would be expected to be greater than on the external surfaces of Wyoming bentonite. The results for the two sodium systems do not show any differences. However, the results for the caesium systems indicate that ion binding is much greater on the external surfaces of Milford saponite than Wyoming bentonite. At the same time, it must be borne in mind that Milford saponite has a higher charge density than Wyoming bentonite. This also favours increased ion association. Furthermore, if the site of charge was of paramount importance, the amount of binding on Fithian illite and Milford saponite surfaces would have been expected to be similar. The results presented in this thesis indicate the importance of charge density in ion binding, but do not allow any firm conclusions to be drawn about the effect of the origin of charge on ion binding.

The present work has led to a greatly increased understanding of the behaviour and distribution of ions at the clay-solution interface. It is obvious that measurements are required on other clay systems to clarify some aspects of this research. Further work is clearly required on silica surfaces and on vermiculite because it has a surface density of charge intermediate between montmorillonite and illite. Studies on the repulsion of cations by positively charged surfaces such as pseudoboehmite and gibbsite could provide valuable information on ion binding as a physical process.

The effect of applied hydrostatic pressure (suction) on the repulsion of chloride by clay surfaces would appear to be a worthwhile extension of the research in this thesis, particularly in view of the proposed ion binding model.

The research discussed here could be extended to ion exchange resins and polyelectrolyte gels, with particular reference to those occurring at the plant root-soil interface. (Jenny and Grossenbacher, 1963). A further field of much interest may lie in physicochemical studies of the ionic distribution in the vicinity of cell walls, which carry negative charges attributable to carboxyl groups of polyuronic acids. (Dainty, Hope and Denby, 1960). Such studies will be particularly relevant in understanding some aspects of ion uptake by plant roots.

The theoretical treatment presented for ion binding is capable of providing a novel approach to the basic aspects of ion exchange isotherms, particularly in view of the concentration dependence of ion association. The availability of such essential nutrients as Ca^{++}, Mg^{++}

and K^+ to plant roots may depend on the average position of the ion with respect to the clay surface. Thus ions present in the soil solution or in the diffuse regions of double layers would be expected to be more readily available for absorption by the plant than those bound in the I.H.P. or the O.H.P. of the clay surface.

The problem concerning the nature and distribution of water in clay-water systems has already been referred to in this thesis. The swelling of these systems may be interpreted more adequately than at present by considering the type and nature of the exchangeable cation. Since in nature, soils are predominantly calcium saturated, particular importance will be attached to the binding of calcium ions at clay mineral surfaces. An especially significant feature of the results is the limited double layer development on calcium illite surfaces, even in dilute suspensions. This is probably the reason for the stability of the domain structure described by Aylmore and Quirk (1960). Further, the particle interaction in such a system must now be interpreted solely in terms of the adsorption of two layers of water by clay surfaces. This type of adsorption occurring in strong salt solutions has been examined in detail by Posner and Quirk (1964). These observations with regard to an illite system are significant because many soils contain this clay mineral.

Perhaps the most important feature of the present work is that the detailed information will allow a more complete approach to the study of clay-water interaction and the associated swelling phenomenon. The full understanding of the structure of clay systems and hence the transport of nutrient ions and water will depend on a fuller appreciation of the mechanisms of swelling. This, in turn, will depend on a complete understanding of the surface properties of these systems.

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APPENDIX I.

Derivation of Overbeek's (1956) Equation for the Fraction of the Particle Charge Compensated by a Deficit of Co-ions

Instead of describing the distribution of ions by the ratio of the concentrations in the double layer regions and the bulk solution, Overbeek (1956) expressed it as the fraction of the surface charge of the colloid, which is compensated by an excess of counterions and a deficit of co-ions respectively. The fraction of the particle charge compensated by a deficit of co-ions is given by

$$\alpha_- = \frac{\int_0^\infty \left[1 - \exp(ze\psi/kT)\right] dx}{\int_0^\infty \left[\exp(-ze\psi/kT) - \exp(ze\psi/kT)\right] dx} \qquad (I.1)$$

where ψ is the potential at a distance x from the surface.

The integral in the numerator of equation (I.1) may be transformed as follows

$$\int_0^\infty \left[1 - \exp(ze\psi/kT)\right] dx = \int_{\psi_0}^{0} \frac{\left[1 - \exp(ze\psi/kT)\right]}{d\psi/dx} d\psi \qquad (I.2)$$

Substituting $d\psi/dx$ from equation (8) leads to

$$\int_{\psi_0}^{0} \frac{\left[1 - \exp(ze\psi/kT)\right] d\psi}{d\psi/dx} = \sqrt{\frac{\varepsilon}{8\pi nkT}} \int_0^{\psi_0} \frac{1 - \exp(ze\psi/kT)\, d\psi}{\exp(ze\psi/kT) - \exp(-ze\psi/kT)}$$

$$= -\sqrt{\frac{\varepsilon}{8\pi nkT}} \int_0^{\Psi_0} \exp(ze\Psi/2kT)\, d\Psi$$

$$= \sqrt{\frac{\varepsilon kT}{2\pi n z^2 e^2}} \left[1 - \exp(ze\Psi_0/2kT) \right] \tag{I.3}$$

The integral in the denominator of equation (I.1) is similarly transformed to give

$$\int_0^{\infty} \left[\exp(-ze\Psi/2kT) - \exp(ze\Psi/kT) \right] dx$$

$$= \sqrt{\frac{\varepsilon kT}{2\pi n z^2 e^2}} \left[\exp(-ze\Psi_0/2kT) - \exp(ze\Psi_0/2kT) \right] \tag{I.4}$$

The fraction of the particle charge compensated by a deficit of co-ions is thus

$$\alpha_- = \frac{1 - \exp(ze\Psi_0/2kT)}{\exp(-ze\Psi_0/2kT) - \exp(ze\Psi_0/2kT)} \tag{I.5}$$

APPENDIX II

London-Van Der Waal Forces.

Diffuse double layer theory does not take into account attractive forces operating between colloidal particles. The only known attractive forces of sufficient generality are the London-van der Waal's forces, which, however, are generally supposed to possess a very short range of influence. Kallmann and Willstatter (1932) suggested that the additivity of these forces may lend them a much longer range. DeBoer (1936) and more especially Hamaker (1936, 1937) used this idea to develop a theory of the stability of lyophobic colloids based on the balance between double layer repulsion and London-van der Waal's attraction. Verwey and Overbeek (1948) used Hamaker's (1937) concept of London-van der Waal's forces to calculate the attractive potential between two large parallel plates of thickness Δ at a distance of separation 2D:-

$$V_A = -\frac{A}{48\pi}\left\{\frac{1}{D^2} + \frac{1}{(D+\Delta)^2} - \frac{2}{(D+\Delta/2)^2}\right\} \text{ergs/cm}^2. \quad \text{(II.1)}$$

A source of considerable controversy has been the value of the London force constant A. Overbeek and Sparnaay (1951, 1952, 1954) measured the attractive forces between two flat glass plates, and obtained a value for $A \simeq 2 \times 10^{-11}$ ergs, which can be compared with their theoretical value of about 10^{-12} ergs. However, the Russian school of Derjaguin and Abricossova (1951, 1953, 1954) obtained a value of $A \simeq 5 \times 10^{-14}$ ergs, by direct measurements of molecular attraction between plane and spherical quartz and glass surfaces in air and in vacuo. In interpreting their results, they criticized the Dutch school for neglecting to take effective precautions against electrostatic effects in their measurements. Derjaguin, Titiyevskaia, Abricossova and Malkina (1954 also suggested that the low sensitivity, low accuracy and poor reproducibility of the measurements were reflected in their results. The problem was resolved by Kitchener and Prosser (1957) who directly measured long range van der Waal's attractive forces between parallel, optically flat glass plates in vacuo. They used a method similar to Overbeek and Sparnaay, but of improved sensitivity, paying particular attention to the elimination of any effects of electric charges on the plates. Their results confirmed the work of Derjaguin and Abricossova that the value of A is 5×10^{-14} ergs.

APPENDIX III

CHLORIDE EXCLUSION BY MONOVALENT FITHIAN ILLITE SYSTEMS

Electrolyte concn. meq./ml.	Wt. of supernatant g.	Wt. of entrained soln. g.	Wt. of clay g.	Total meq. Cl^- in supernatant	Total meq. Cl^- in entrained soln.	Cl^- exclusion ml./g.
LITHIUM						
.4472	9.564	1.133	.456	4.2541	0.4808	0.114
.2683	8.850	1.298	.456	2.3705	0.3313	0.091
.0894	8.717	1.284	.456	0.7847	0.1075	0.202
.0266	9.450	1.480	.456	0.25543	0.03572	0.351
.0091	9.023	2.083	.456	0.08385	0.01709	0.549
SODIUM						
.5026	9.424	1.113	.503	4.6682	0.5282	0.091
.3010	8.910	1.234	.503	2.6654	0.3525	0.107
.0999	9.122	1.292	.504	0.9143	0.1226	0.139
.0300	9.464	1.406	.504	0.28771	0.03866	0.268
.0104	8.795	1.815	.504	0.09267	0.01710	0.389
POTASSIUM						
.5030	9.374	1.256	.497	4.6268	0.6080	0.048
.3043	9.174	1.229	.497	2.7603	0.3636	0.040
.1009	9.529	1.252	.497	0.9613	0.1220	0.084
.0302	9.404	1.422	.497	0.28569	0.04109	0.141
.0103	8.991	1.597	.497	0.09372	0.01558	0.205
.0031	8.264	2.110	.498	0.02620	0.00593	0.492

CHLORIDE EXCLUSION BY MONOVALENT FITHIAN ILLITE SYSTEMS

Electrolyte concn. meq./ml.	Wt. of supernatant g.	Wt. of entrained soln. g.	Wt. of clay g.	Total meq. Cl^- in supernatant	Total meq. Cl^- in entrained soln.	Cl^- exclusion ml./g.
RUBIDIUM						
.5070	9.895	1.382	.506	4.8228	0.6727	0.004
.3042	9.455	1.340	.506	2.8088	0.3949	0.020
.1018	9.490	1.319	.506	0.9601	0.1319	0.030
.0106	9.004	1.507	.506	0.09603	0.01572	0.060
.0032	9.215	1.604	.506	0.02924	0.00491	0.115
CAESIUM						
.5048	10.098	1.751	.533	4.8207	0.8363	0.000
.3043	9.278	1.778	.533	2.7209	0.5262	-0.032
.1027	9.006	1.751	.533	0.9131	0.1783	-0.013
.0305	9.304	1.691	.533	0.28316	0.05202	-0.038
.0105	8.818	1.738	.533	0.09284	0.01814	0.028
.0032	8.847	1.846	.533	0.02796	0.00585	-0.011
AMMONIUM						
.4837	9.404	1.343	.514	4.5238	0.6333	0.033
.2899	9.655	1.325	.514	2.7927	0.3767	0.047
.0972	9.198	1.437	.513	0.8953	0.1368	0.060
.0290	9.280	1.612	.514	0.27061	0.04503	0.128
.0098	9.156	1.756	.514	0.09206	0.01702	0.128

CHLORIDE EXCLUSION BY MONOVALENT WYOMING BENTONITE SYSTEMS

Electrolyte conc. meq./ml.	Wt. of supernatant g.	Wt. of entrained soln. g.	Wt. of clay g.	Total meq. Cl^- in supernatant	Total meq. Cl^- in entrained soln.	Cl^- exclusion ml./g.
LITHIUM						
.4516	12.209	8.664	.424	5.5326	3.7989	0.665
.2706	11.863	8.543	.425	3.2408	2.2449	0.771
.0265	8.935	12.206	.424	0.2480	0.3116	2.43
.0101	11.024	15.059	.424	0.11837	0.14453	4.01
.0030	17.370	8.429	.424	0.07151	0.00594	6.92
POTASSIUM						
.5086	16.535	3.990	.430	8.2561	1.9561	0.167
.3039	15.792	5.254	.430	4.7653	1.5449	0.311
.1011	13.317	6.891	.430	1.3582	0.6775	0.586
.0299	13.376	7.249	.430	0.4117	0.2058	1.34
.0098	12.089	8.570	.430	0.12461	0.07779	2.52
.0029	14.614	6.873	.430	0.04550	0.01690	3.61
CAESIUM						
.4971	9.405	1.010	.504	4.3996	0.4568	0.064
.3066	16.838	4.558	.519	4.9908	1.3357	0.096
.0993	20.069	2.737	.522	2.0021	0.2623	0.213
.0593	20.198	5.124	.526	1.2071	0.2935	0.418
.0186	19.740	5.007	.526	0.37144	0.08845	0.591
.0144	19.456	3.929	.522	0.28511	0.05228	0.699
.0100	19.740	4.528	.496	0.19798	0.04174	0.840
.0049	8.900	0.999	.501	0.04639	0.00291	1.14
.00374	19.865	5.140	.541	0.07629	0.01722	1.25

CHLORIDE EXCLUSION BY MONOVALENT MILFORD SAPONITE SYSTEMS

Electrolyte concn. meq./ml.	Wt. of supernatant g.	Wt. of entrained soln. g.	Wt. of clay g.	Total meq. Cl^- in supernatant	Total meq. Cl^- in entrained soln.	Cl^- exclusion ml./g.
SODIUM						
.3560	13.023	4.479	.345	4.6804	1.5524	0.479
.0981	10.859	6.794	.343	1.0906	0.6429	1.200
.0499	6.178	13.915	.346	0.3159	0.6844	1.462
.0101	13.880	6.062	.344	0.15074	0.05067	4.15
.0050	14.348	5.678	.347	0.07972	0.02041	5.98
CAESIUM						
.0291	9.232	0.730	.301	0.26991	0.02003	0.153
.01011	9.226	0.744	.299	0.09413	0.00664	0.304
.00306	8.998	0.927	.295	0.02806	0.00230	0.654
.00103	9.266	0.707	.294	0.00983	0.00046	0.977

CHLORIDE EXCLUSION BY DIVALENT FITHIAN ILLITE SYSTEMS

Electrolyte concn. meq./ml.	Wt. of supernatant g.	Wt. of entrained soln. g.	Wt. of clay g.	Total meq. Cl⁻ in supernatant	Total meq. Cl⁻ in entrained soln.	Cl⁻ exclusion ml./g.
MAGNESIUM						
.4999	9.705	1.005	.529	4.7899	0.4737	0.083
.2997	9.599	0.922	.529	2.8586	0.2606	0.089
.1007	9.059	0.981	.529	0.9109	0.0968	0.034
.0300	9.549	0.974	.529	0.28710	0.02874	0.032
.0103	9.135	0.979	.529	0.09461	0.01003	0.023
.0031	9.250	1.087	.528	0.02788	0.00373	-0.278
CALCIUM						
.4688	9.044	0.970	.569	4.1758	0.4273	0.076
.2819	9.095	0.948	.569	2.5424	0.2535	0.069
.1002	8.467	0.850	.569	0.8512	0.0790	0.112
.0280	8.810	0.994	.569	0.24794	0.02692	0.070
.0028	8.824	1.034	.569	0.02518	0.00249	0.288
BARIUM						
.4800	9.339	0.903	.466	4.3556	0.4091	-0.036
.2958	9.281	0.771	.466	2.6707	0.2273	-0.036
.0977	9.008	0.864	.466	0.8764	0.0827	0.028
.0292	9.025	0.873	.466	0.26342	0.02520	0.021
.0102	9.437	0.884	.466	0.09626	0.00927	-0.054

CHLORIDE EXCLUSION BY STRONTIUM AND ALUMINIUM FITHIAN ILLITES

Electrolyte concn. meq./ml.	Wt. of supernatant g.	Wt. of entrained soln. g.	Wt. of clay g.	Total meq. Cl^- in supernatant	Total meq. Cl^- in entrained soln.	Cl^- exclusion ml/g.
STRONTIUM						
.5067	9.044	0.913	.553	4.4232	0.4525	-0.022
.3031	9.710	0.986	.553	2.8939	0.2869	0.042
.1013	9.282	1.050	.554	0.9341	0.1055	0.004
.0104	9.155	0.977	.553	0.09553	0.01001	0.033
ALUMINIUM						
.4286	9.147	1.313	.511	3.8404	0.5707	-0.088
.2574	9.065	1.352	.511	2.2899	0.3657	-0.184
.0877	9.036	1.367	.510	0.7673	0.1417	-0.572
.0269	8.798	1.454	.510	0.22173	0.05374	-1.25
.0094	8.655	1.509	.510	0.07454	0.02143	-1.75
.0029	8.537	1.556	.511	0.02113	0.00768	-2.62

APPENDIX IV

ALUMINIUM RELEASE FROM FITHIAN ILLITE AND WYOMING BENTONITE ON WASHING WITH 1 MOLAR NaCl at pH 3.0

	Fithian Illite		Wyoming bentonite	
Wash Number	pH	Al release meq./100 g.	pH	Al release meq./100 g.
1	6.2	-	6.7	0.05
2	5.9	0.01	6.3	0.05
3	5.0	0.01	4.9	0.08
4	4.7	0.02	4.5	0.04
5	4.2	0.02	4.0	0.06
6	3.6	0.02	3.9	0.11
7	3.4	0.06	3.9	0.16
8	3.3	0.04	3.5	0.13
9	3.2	0.06	3.3	0.16
10	3.2	0.05	3.3	0.19
Total Al^{+++} release		0.29*		1.03*

* In each case, total Al^{+++} release during the standard state preparation procedure was approximately 1% of the exchange capacity. (Fithian Illite 30 meq./100 g; Wyoming bentonite 93 meq./100 g.)

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