THE FORMATION AND SWELLING OF COMPLEXES BETWEEN MONTMORILLONITE AND SOME ORGANIC COMPOUNDS

A thesis submitted

by

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PREFACE

This 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 my knowledge and belief, contains no material previously published or written by another person, except when due reference is made in the text of the thesis.

B.K.G. Theng

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INTRODUCTION

Organic matter has been described as the key to soil fertility since it affects both the chemical and physical properties of the soil. A considerable amount of evidence has been presented to show that organic matter exerts a beneficial effect on the structure of the soil. The striking results obtained using synthetic soil conditioners have led to the postulate that the polymeric substances of soil organic matter are responsible for increasing the water-stability of natural soil aggregates. However, the processes by which these substances improve aggregation are still not clearly understood.

Organic compounds adsorbed onto clay surfaces are thought to stabilize soil aggregates in two ways. Firstly, they strengthen the coarse pores within the aggregate so that water moves in a controlled fashion from these pores to the remainder of the pore space (Panabokke and Quirk, 1957). Cultivated aggregates which lack the presence of organic strengthening materials have been shown to develop planes of failure, when wet, causing the water to advance rapidly along such planes. The presence of failure planes predisposes the aggregate to slake in water and this is referred to as incipient failure (Quirk and Panabokke, 1962). Secondly, adsorbed organic compounds may control particle-particle interaction by modifying surface adsorption of water. This mechanism would result in less swelling.

The aim of the present work is to study the adsorption of organic compounds by clays and the manner in which these compounds control the swelling of clay systems.

Organic compounds may control the swelling of clay systems by two different mechanisms,

(i) It is known that the hydration and swelling of clay systems saturated with inorganic cations are controlled by the hydration energy of the ions and by the ability of the ions to dissociate from the clay surface. Organic cations are adsorbed onto clay surfaces by an ion-exchange mechanism thereby modifying the forces operative at the clay surface and thus the swelling properties of the system. It has been reported by Emerson (1962) that adsorption of cetyltrimethylammonium bromide needs only be on external crystal surfaces to greatly reduce swelling.

(ii) The manner in which organic polymers control swelling is by interparticle bonding or cross-linking in which a polymer molecule is attached to several clay or soil particles. In addition to interparticle bonding the polymer molecule, when introduced into an already aggregated system, may spread over adjacent clay surfaces. This increases the strength of the pores within the aggregate and thus the ability of the aggregate to withstand rapid wetting.

The swelling of complexes between montmorillonite and alkylammonium compounds and between montmorillonite and polyvinyl alcohols has therefore been studied.

Swelling measurements reported in this thesis were carried out on compressed clay systems and it is essential to separate the water held by physico-chemical forces at the clay surface from that water which is simply enmeshed within the gel structure (Aylmore and Quirk, 1959). Incipient failure of soil aggregates on rapid wetting may be considered as being due to the creation of a gel structure which supports the retention of large amounts of water by surface tension forces.

To understand how organic compounds control swelling, the adsorption mechanisms must be fully understood. Considerable attention has therefore been given to the processes by which organic compounds are adsorbed by clays.

Montmorillonite was used as the clay material. The interlamellar swelling of this material saturated with inorganic cations has been studied in detail by X-ray diffraction techniques (Norrish, 1954). It is thought that the same methods can be applied to complexes between montmorillonite and organic cations. Information obtained by such methods can be related to that obtained from swelling measurements on compressed clay systems.

A homologous series of alkyl-substituted ammonium compounds were chosen as adsorbate materials. The structures of these compounds are well known and the orientation and molecular conformations of the adsorbed molecules can be studied by chemical, X-ray diffraction and infra-red spectroscopy methods. Of the polymeric materials suitable for study, polyvinyl alcohol was chosen for the present work. It has been shown that polyvinyl alcohol is extremely effective in increasing the mechanical strength and water-stability of natural soil aggregates (Emerson, 1956; Williams, 1959). An added advantage in choosing polyvinyl alcohol is that the adsorption of this uncharged linear polymer from aqueous solution onto clays has been studied in some detail (Greenland, 1963).

The thesis is divided into six chapters. Chapter I contains a review of the relevant literature on clay-water interaction, mechanisms of adsorption and modification of swelling of clays by adsorption of organic cations and polymers. The formation of complexes between montmorillonite and alkylammonium compounds is described in Chapter II. Structural studies of the complexes by X-ray diffraction and infra-red spectroscopy methods form the subject matter of Chapter III. The effect of adsorbed alkylammonium compounds and polyvinyl alcohol on the swelling of montmorillonite is presented in Chapters IV and V, respectively. Finally, in Chapter VI the general conclusions are summarized and discussed.

CHAPTER I.

REVIEW OF THE LITERATURE

I. 1. Structure of Montmorillonite

I. 1. 1. General

The pioneering work of Pauling (1930) and of Jackson and West (1930, 1933) in elucidating the atomic structure of mica and related minerals has considerably contributed towards the understanding of the structural properties of clay minerals.

In 1933, Hofmann, Endell and Wilm proposed a lattice structure for montmorillonite which is essentially similar to that for the mineral pyrophyllite but having a variable *c*-axis depending on the water content of the system. The unit lamellae making up a crystal were thought to be stacked in a regular periodicity in the direction of the *a*-and *b*-axis. Maegdefrau and Hofmann (1937) modified the structure, as originally proposed, by suggesting that the stacking of the individual lamellae occurred in a random fashion giving rise to a turbostratic arrangement.

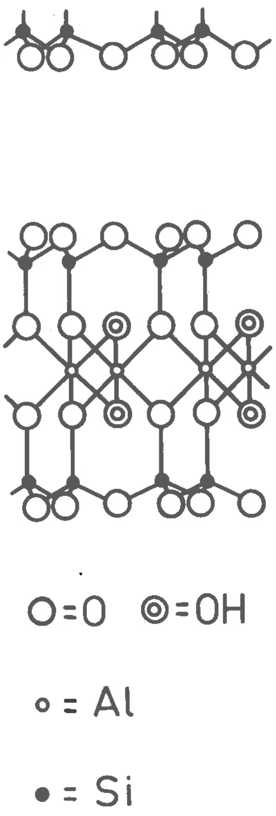
The lattice structure of pyrophyllite consists of an alumina octahedral layer sandwiched between two silica tetrahedral sheets (Figure 1*a*). The aluminium atom is octahedrally co-ordinated to oxygen atoms and hydroxyl groups which constitute the two closely packed central layers of the lattice. The silicon atom is tetrahedrally co-ordinated to oxygen atoms. The Si-O tetrahedra share their vertices with the octahedral layer whilst their basal oxygen atoms are arranged in an open hexagonal network.

Figure 1*a*.

Structure of pyrophyllite (diagrammatic) viewed along the *a*-axis.

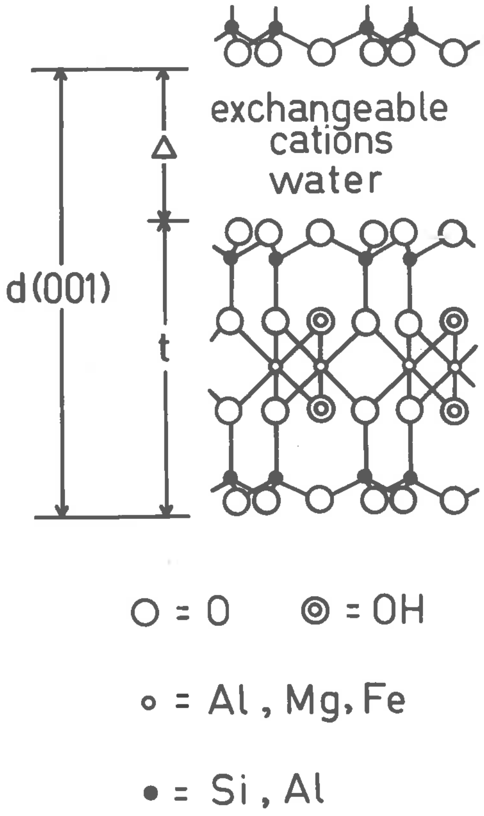
Figure 1*b*.

Structure of montmorillonite (diagrammatic) viewed along the *a*-axis.



Structure of Pyrophyllite

Figure 1a



Structure of Montmorillonite

Figure 1b

Radoslovich (1960) and Radoslovich and Norrish (1962) have proposed that for most layer lattice silicates the open hexagonal network is distorted by the opposed rotation of alternate silica tetrahedra, resulting in a ditrigonal surface configuration. This rotation is attributed to a misfit between the larger tetrahedral layer and the smaller octahedral layer. It is further proposed that in all layer silicates the Si-O tetrahedra can rotate readily to reduce the dimension of this tetrahedral layer. The average rotational angle, α, may be predicted from the observed <u>b</u>-axis if the frequency of isomorphous replacement of Si by Al in the tetrahedral layer is known.

I. 1. 2. <u>Structure of Montmorillonite</u>

The name montmorillonite was originally used for a clayey material having the approximate composition of

$$4\ SiO_2.Al_2O_3.(1+x)\ H_2O$$

where x is the number of water molecules which can be reversibly removed by heating at a low temperature (Damour and Salvétat, 1847, quoted by MacEwan, 1961). The term montmorillonite is now used to denote either a whole group of hydrated silicates having similar X-ray diffraction patterns to montmorillonite or a member of this group which has approximately the same chemical composition as the material of Damour and Salvétat (MacEwan, 1961). The name montmorillonite has also been used to denote the dioctahedral member of the montmorillonite (smectite) group having a Si:Al ratio of about 5:2. Other members in the group are beidellite, nontronite, hectorite, and saponite (Ross and Hendricks, 1945; Grim, 1953). Recently, Greene-Kelly (1955a) has suggested that the term montmorillonite be used for those minerals of the group in which the charge deficiency mainly arises from isomorphous replacement in the octahedral layer.

The montmorillonite lattice differs from that of pyrophyllite in the following ways (Marshall, 1935; Hendricks, 1942).

(i) Lattice substitution of magnesium, iron, etc. for aluminium in octahedral co-ordination and of aluminium for silicon in the tetrahedral layer, always occurs.

(ii) As a consequence of substitution within the lattice or isomorphous replacement, the lattice is not electrically neutral. Some internal compensating substitutions may take place, but the final result is always a lattice which carries a permanent negative charge. The charge deficiency of the lattice is balanced by exchangeable cations.

(iii) Water and other polar molecules can enter between the individual lamellae of the crystal (intercalation) causing the crystal to expand in the direction of the c-axis (intracrystalline or interlamellar swelling).

The structure of montmorillonite is shown diagrammatically in Figure 1b.

The thickness of the montmorillonite lamella (denoted by t in Figure 1b) is obtained by adding the distance from the centre of one sheet of oxygen atoms to the other to twice the van der Waals radius of oxygen, (MacEwan, 1948b, Greene-Kelly, 1955b). The calculated thickness is 9.40 Å if it is assumed that the montmorillonite lamella has the muscovite structure and the van der Waals radius of oxygen is taken as 1.40 Å (Pauling, 1960, p. 260). On heating *in vacuo* montmorillonite saturated with inorganic cations of different size gives a minimal d(001) or basal spacing of 9.5 Å. This value can be regarded as the effective thickness of the montmorillonite lamella and is independent of the radius of the exchangeable cation, provided that it does not exceed 1.2 Å (Greene-Kelly, 1955*b*). The nature of the cation involved in lattice substitution and the frequency of isomorphous replacement within the pyrophyllite lattice give rise to a series of mica type minerals of different surface charge density. The surface density of charge of a given clay mineral can be defined as the number of unit charges per unit area and is an important parameter since it determines the force holding the clay lamellae together (see I. 2. 4.).

I. 2. Interaction between Clays and Water

I. 2. 1. Introduction

A clay mass is thought to be made up of regions of oriented clay particles, interspersed by pores or capillaries, and thus bears a close resemblance to a natural soil aggregate.

The water adsorbed by a clay mass may be directly associated with the surface of the clay particles (surface adsorption) or may be retained in the pore spaces by surface tension forces (capillary condensation). Surface adsorption of water by cations results in particle re-arrangement. Both this re-arrangement and increased separation of clay lamellae or crystals to accommodate further adsorption of water lead to an increase in the volume of the system. This increase is referred to as swelling. However, particle interaction does not always lead to an increase in volume (swelling) because this interaction may be accommodated within the pores of the system and hence this type of interaction may be referred to as internally accommodated swelling because there is no external manifestation of the volume change. However, the physical properties of the system may be greatly altered as a result of this interaction.

These three categories of adsorbed water are not readily distinguished quantities. Surface adsorption, capillary condensation, and swelling are concomitant and to a certain extent co-operative processes.

I. 2. 2. Surface Adsorption

Considerable attention has been given to the properties of water adsorbed at and near clay surfaces. Due to the mutual attraction between the water dipoles and the polarizing effect of the negatively charged clay surface the adsorbed water possesses different physical properties from those of ordinary liquid water. The thickness of the adsorbed water is still open to some uncertainty but may possibly extend to ten molecular layers. The properties of the adsorbed water have been reviewed and discussed in detail by Martin (1960) and by Low (1961).

Many workers have postulated that the water in the vicinity of clay surfaces has an ordered arrangement. Basing their arguments on the association of water molecules in tetrahedral arrangement as proposed by Bernal and Fowler (1933), Hendricks and Jefferson (1938) considered that the water molecules formed a regular hexagonal network with the six oxygen atoms coplanarly situated at each corner of the hexagon. At alternate corners, the atoms were hydrogen-bonded to the oxygens of the subjacent silicate surface. The Hendricks-Jefferson model has been criticised by a number of workers (Hofmann and Hausdorf, 1942; Walker, 1949) as it did not take into account the influence of the exchangeable cations. Mackenzie (1950) has presented data to show that at low water contents surface adsorption is primarily dependent on the nature of the exchangeable cation, the clay surface being of relatively subsidiary importance. Other evidence for the determining effect of the exchangeable cation on the geometrical arrangement of surface water has been provided by Mathieson and Walker (1954). These workers have made a single crystal X-ray analysis of Mg^{++} vermiculite. Specific positions were assigned to the interlamellar water molecules with respect to the magnesium ion and to adjacent silicate lamellae. It was proposed that the exchangeable magnesium ion holds the water networks together to form hydration shells around the cation. The water molecules were arranged in a hexagonal network by weak hydrogen bonding to the surface oxygens of the clay lamellae.

The initial water to be adsorbed at clay surfaces would therefore appear to be associated with the exchangeable cations. The situation in which the adsorbed water is present as a single layer covering the clay surface (monolayer adsorption) has received particular attention. A number of workers (Mooney, Keenan and Wood, 1952a and b; Goates and Hatch, 1953; Orchiston, 1953, 1954, 1955) have applied the adsorption equation due to Brunauer, Emmett and Teller (1938) for the multimolecular adsorption of gases and vapours onto solid surfaces, to water vapour sorption data to obtain an estimate of the surface areas of clays and soil colloids.

The general form of the Brunauer, Emmett and Teller (B.E.T.)

isothermal equation, derived from kinetic considerations, is

$$V = \frac{V_m cx}{1 - x} \cdot \frac{1-(n + 1)\, x^n + nx^{n + 1}}{1 + (c - 1)x - cx^{n + 1}} \qquad \text{......(1)}$$

where V is the volume of gas or vapour adsorbed at a particular relative pressure x, V_m is the volume adsorbed at monolayer conditions, n is the number of layers of gas or vapour adsorbed and c is a constant such that

$$c \simeq \exp.\ (E_1 - E_L) / RT \qquad \text{......(2)}$$

E_1 being the energy of adsorption of the monolayer and E_L that of successive layers and equals the energy of liquefaction (condensation).

Putting n = 1, equation (1) reduces to

$$V = \frac{V_m\, cx}{1 + cx} \qquad \text{......(3)}$$

and writing P/P_o for x we obtain

$$\frac{P}{V} = \frac{P_o}{V_m c} + \frac{P}{V_m} \qquad \text{......(4)}$$

which is the well-known Langmuir equation (1916, 1918).

For values of $n \longrightarrow \infty$, or for $x < 0.4$ and $n > 4$ equation (1) can be written as

$$\frac{P/P_o}{V\ (1-P/P_o)} = \frac{1}{V_m c} + \frac{c - 1}{V_m\ c} \cdot P/P_o \qquad \text{......(5)}$$

In this form, a plot of the left-hand term against P/P_o gives a straight line from which the parameters of V_m and c can be evaluated from the slope and the Y-intercept. The surface area of the adsorbent can readily be obtained from the calculated value of V_m and the area occupied by a single adsorbate molecule. The uncertainty pertaining to the nature of the adsorbent surface, the orientation of the adsorbed molecules and the distortion of bond angles of the molecules on adsorption make precise determination of molecular areas rather difficult. It is generally assumed that the adsorbed molecules are in hexagonal close packing. Under these conditions the area occupied by a single molecule may be estimated from the relationship,

$$D_m = 1.33 \left(\frac{M}{d}\right)^{1/3} \times 10^{-8} \qquad \ldots\ldots(6)$$

where D_m is the molecular diameter in Ångstrom units, M is the molecular weight and d the density of the adsorbate. Values for the area of a single nitrogen and water molecule obtained from equation (6) are 16.2 and 10.8 $Å^2$, respectively.

The application of equation (5) to water vapour sorption data has led to the conclusion that for water and other polar molecules the term monolayer in the original sense of Brunauer, Emmett and Teller, is not strictly applicable (Mooney, Keenan and Wood, 1952 a and b; Quirk, 1955). Water molecules are more strongly attracted to the exchangeable cations than to the clay surface and therefore tend to form clusters around the cations. For a particular clay material this effect of the cation on the arrangement of water molecules in the first layer is dependent on the valency and size of the cation. Quirk (1955) has compared the data for surface areas of clays obtained from water vapour sorption studies ("water" areas) to those obtained from low temperature van der Waals adsorption of nitrogen ("nitrogen" areas). It was concluded that the "water" areas were dependent on the surface density of charge of the clay mineral but that the B.E.T. equation was obeyed because the basic requirement that the first layer of molecules was adsorbed with a considerably larger energy than that of subsequent layers, was fulfilled.

The adsorption of non-polar molecules such as nitrogen is not dependent on the exchangeable cations and surface density of charge of the clay. Neglecting such effects as surface irregularities and distortion of bond angles of the adsorbed molecules, a "true" monolayer of closely packed nitrogen molecules is formed over the entire accessible surface.

With expanding lattice minerals, such as montmorillonite, a further complication arises due to the fact that the water molecules are able to enter between the individual lamellae within a crystal (intercalated). The "monolayer" value, in this instance, represents the amount of water sorbed onto both inter- and intracrystalline surfaces with the difference that in the latter instance the "monolayer" is shared between two opposing surfaces. Nitrogen molecules, on the other hand, are not intercalated by montmorillonite and specific areas calculated from low temperature van der Waals adsorption of nitrogen therefore represent the external or intercrystalline surfaces only.

I. 2. 3. Capillary Condensation

Multilayer adsorption of water vapour is followed by capillary condensation when the relative vapour pressure is raised.

The fundamental equation describing this process is the Kelvin equation. On the adsorption branch of the isotherm, the pores are filled at a relative pressure P_a/P_o, given by

$$P_a/P_o = \exp.\ \left(- \frac{\Upsilon v}{RTr}\ .\ \cos\theta\right) \qquad \ldots\ldots(7)$$

while the pores are emptied on the desorption branch of the isotherm when the relative pressure reaches the value, given by

$$P_d/P_o = \exp.\ \left(- \frac{2\Upsilon v}{RTr}\ .\ \cos\theta\right) \qquad \ldots\ldots(8)$$

where P_a and P_d are the adsorption and desorption pressures, respectively and P_o is the saturation vapour pressure; Υ is the surface tension of the liquid, v is the molar volume and T is the absolute temperature; R is the gas constant, r is the radius of the hemispherical meniscus (Kelvin radius) and θ is the angle of contact. It is usual to take $\cos\theta = 1$, that is, to assume that the contact angle is zero.

If cylindrical pores are assumed, the average radius of the pores can be obtained from

$$\bar{r} = \frac{2\ V_p}{S} \qquad \ldots\ldots(9)$$

where V_p stands for the pore volume or porosity of the system and S is the total surface area.

The basic assumption of the Kelvin equation is that all "adsorption" is entirely due to capillary condensation. This condition is certainly not fulfilled in the case of the adsorption of water by clays, since formation of adsorbed layers begins before capillary condensation is manifested and must continue at the surface of the unfilled pores. To obtain a more realistic theory, a correction must be introduced for the adsorbed layers.

Innes (1957) has proposed a modified form of the Kelvin equation which takes into account the thickness of the adsorbed film in a situation where a cylindrical rather than an hemispherical meniscus is present. This equation is written as

$$d - 2t = \frac{2\gamma M}{RT \ \ln P/P_o} \qquad \ldots\ldots(10)$$

where t is the thickness of the adsorbed film, d is the maximum distance between parallel plates (or crystals) at which capillary evaporation can occur at a given relative pressure P/P_o and M is the molecular weight of the liquid. Equation (10) has been used by Aylmore and Quirk (1962) to obtain the pore size distribution of compressed clay cores from the desorption branch of the liquid nitrogen isotherm.

Hysteresis in the vapour pressure-liquid content relationship of porous solids has been attributed to a delay in the refilling of the air-filled porosity on wetting, that is, to a hysteresis in γ or to the presence of "ink-bottle" pores (Katz, 1949). The latter is a blockage effect of the smaller capillaries which may stay filled during the desorption process thus preventing the connecting larger pores from being emptied. Recently, de Boer (1958) has put forward a theory whereby the shape of the pores may be derived from the shape of the hysteresis loop. However, as has been pointed out by Schofield (1938) and later confirmed by Holmes (1955), hysteresis phenomena could occur in systems where air-liquid interfaces were absent. Working with moulded clay blocks, Holmes (1955) has concluded that in these systems, most of the hysteresis observed in the suction-water content relationship was due to plastic readjustments of the clay particles with respect to each other rather than to a delay in the formation of a meniscus. The existence of a large number of independent domains in the systems has also been postulated to account for hysteresis phenomena by Everett and Whitton (1952).

I. 2. 4. Swelling

The swelling of a given clay mass - neglecting the effect of particle re-arrangement - can be due to an increase in separation between individual lamellae making up a crystal (interlamellar or intracrystalline swelling) and/or between individual crystals (intercrystalline swelling). Clays which show the former type of swelling, for instance montmorillonite and vermiculite, are referred to as expanding lattice type minerals as opposed to non-expanding lattice minerals in which intracrystalline swelling is absent.

Since the direct X-ray approach can be used to measure the interlamellar expansion in montmorillonite (and vermiculite), our knowledge of the mechanism of swelling of clays has mainly been obtained from studies on the intracrystalline swelling of these clay materials and therefore this will be discussed in detail.

Intracrystalline swelling can be further divided into two more or less distinct processes, limited and extensive crystalline swelling.

(i) Intracrystalline swelling

a. Limited crystalline swelling

Hofmann, Endell, and Wilm (1933) were the first to observe that water was able to diffuse between the lamellae making up a crystal of montmorillonite causing the crystal to expand in the direction of the c-axis. Limited crystalline swelling can therefore be regarded as a surface adsorption process whereby successive water layers are formed in the interlamellar region.

A number of workers (Bradley, Clark and Grim, 1937; Hendricks, Nelson and Alexander, 1940) have used X-ray diffraction techniques to study the relationship between the amount of water adsorbed at different values of relative pressure and the interlamellar separation in montmorillonite. It was concluded that the interlamellar spacing increased in a stepwise fashion up to a maximum of four layers of water molecules. This conclusion has been confirmed by Mooney, Keenan and Wood (1952b) and by Norrish (1954) and it is therefore considered that limited crystalline swelling does not proceed beyond a basal spacing of about 22 Å corresponding to four water layers.

The water taken up initially is undoubtedly due to the hydration of the interlamellar cations. The repulsive energy due to ion hydration is opposed by the coulombic attraction between the cations and the negatively charged clay lamellae.

Considering the cation as a point charge situated at a given distance from the silicate surface which is regarded as a plane conductor, Norrish (1954) has derived the following relationship between the attractive potential (E_a), the valency (v) and the surface density of charge (σ) of the clay,

$$E_a = \frac{\sigma v e}{2 D \varepsilon} \qquad \text{......(11)}$$

where e is the electronic charge, ε is the dielectric constant of the medium. D is the half-distance between two opposing parallel lamellae, so that

$$D = \frac{[d(001) - 9.5]}{2} \times 10^{-8} \text{ cm} \qquad \ldots\ldots(12)$$

where the value of 9.5 is the assumed thickness of the silicate lamella.

The interlamellar cation can also be considered as a point charge situated between the plates of a condenser. In this instance the attractive potential is given by

$$E_a' = \frac{2\pi \sigma^2 D}{\varepsilon} \quad \text{erg/cm}^2 \qquad \ldots\ldots(13)$$

The actual attractive force is probably a compromise between E_a and E_a'. The repulsive potential, E_r, is provided by the hydration energy of the interlamellar cation, and is given by

$$E_r = \frac{2\,U\sigma}{v\,e\,N} \times 4.186 \,.\, 10^{10} \text{ erg/cm}^2 \qquad \ldots\ldots(14)$$

where U is the total hydration energy of the cation in kcal/gram ion and N is Avogadro's number.

If the attractive potential is taken as that given by equation (13), the ratio of E_r/E_a' can be regarded as an index of the swelling ability of the clay. Since this index is inversely proportional to σ, the magnitude of the surface density of charge for a given clay mineral will determine the limited crystalline swelling of the clay. Table 1 summarizes the limited crystalline swelling of a number of clay minerals structurally similar to montmorillonite as a function of the surface density of charge of the mineral and the nature of the interlamellar cation.

TABLE 1 (Norrish, 1954)

Effect of surface density of charge on the maximum value of basal spacing (Å) in limited crystalline swelling.

Interlamellar cation	Mineral	Pyrophyllite	Montmorillonite	Vermiculite	mica	brittle mica
	σ (e.s.u./cm^2)	0	3×10^4	$\sim 6 \times 10^4$	10^5	2×10^5
Li^+		no interlamellar cation no swelling	22.0	15.0		
Na^+			19.0	14.8	14.3	
Al^{+++}			19.0	14.0		
Mg^{++}			19.0	14.6	14.3	
Ca^{++}			19.0	15.4		10
Ba^{++}			19.0	15.4		
K^+			15.0	~ 11.0	10.0	
NH_4^+			15.0	~ 11.0		
Cs^+			13.8	12.0		

For any cation the limited crystalline swelling is increased as σ decreases from 2×10^5 e.s.u./cm^2 for brittle mica to 3×10^4 e.s.u./cm^2 for montmorillonite. However, if the surface charge density of montmorillonite is greatly decreased by introducing lithium ions into the lattice, swelling is decreased (Quirk and Theng, 1960).

b. Extensive crystalline swelling.

If the hydration energy of the interlamellar cation is sufficiently large the potential barrier of attractive forces is overcome and intracrystalline swelling passes from a limited to an extensive crystalline swelling. This transition is evidenced by an explosive expansion of the basal spacing from 20 Å to > 30 Å after which interlamellar expansion is only dependent on the external electrolyte concentration (C). It has been shown that a linear relationship exists between interlamellar separation of montmorillonite saturated with small monovalent cations (H^+, Li^+, Na^+) and $C^{-\frac{1}{2}}$ (Norrish, 1954).

The Gouy-Chapman theory of diffuse double layers has been applied to describe the extensive crystalline swelling of montmorillonite (Norrish, 1954). In this view the retention of large amounts of water in the interlamellar region is attributed to the osmotic repulsion of interacting double layers. Since for any given concentration of electrolyte an equilibrium interlamellar spacing is attained, the repulsive potential must be balanced by an opposing attractive potential of the same magnitude. One source of attraction is provided by long-range van der Waals forces.

The van der Waals attractive potential, V_A, for two parallel lamellae of thickness δ and separated by a distance 2D from each other, is given by the following relationship (Verwey and Overbeek, 1948, p. 101).

$$V_A = -\frac{A}{48\pi}\left[D^{-2} + (D + \delta)^{-2} - (D + \frac{\delta}{2})^{-2}\right] \qquad \ldots\ldots(15)$$

where A is the van der Waals constant ($\simeq 10^{-12}$ ergs). The above relationship may not be valid for plate separations greater than 400 Å for which V_A becomes approximately proportional to D^{-4} (Norrish and Rausell-Colom, 1961).

The repulsive potential, V_R, due to interacting double layers derived from the Gouy-Chapman double layer equation takes the form (Verwey and Overbeek, 1948, p. 95).

$$V_R = \frac{64\ nkT}{K} \ .\ p^2\ .\ \exp.\ (-2\ KD) \qquad \ldots\ldots(16)$$

where n is the number of cations per ml, k is the Boltzmann constant and T is the absolute temperature. K is the reciprocal of the Debye characteristic length and defined as

$$K^2 = \frac{8\pi n\ e^2\ v^2}{k\ T\ \varepsilon} \qquad \ldots\ldots(17)$$

p is defined as

$$p = \frac{\exp.\ (z/2) - 1}{\exp.\ (z/2) + 1} \qquad \ldots\ldots(18)$$

where $z = \frac{ve\ \psi_o}{kT}$, ψ_o being the electric potential at the clay surface.

When actual values of V_A and V_R are computed by applying equations (14) and (15) for each equilibrium interlamellar spacing, the resulting potential curve of interaction shows an appreciable net repulsion (Norrish, 1954; van Olphen, 1962; Norrish and Rausell-Colom, 1961). The discrepancy between V_R and V_A increases as the electrolyte concentration is lowered, that is, as the interlamellar separation increases.

To account for the discrepancy, van Olphen (1953) has suggested that the interlamellar cations were specifically adsorbed onto the clay surface. Since this discrepancy diminishes with increasing electrolyte concentration, the magnitude of the specific adsorption forces would also have to decrease progressively as the concentration is increased. Such a dependence of these forces on the electrolyte concentration is difficult to envisage. Another source of attraction is thought to be provided by edge-to-face links between clay lamellae (van Olphen, 1962; Norrish and Rausell-Colom, 1961). These links were thought to arise as a result of electrostatic attraction between the negatively charged planar surface and the positive charges at the edges of the lamella. The existence of positive charges on kaolinite is now well-established (Schofield and Samson, 1954; Quirk, 1956). Norrish and Rausell-Colom (1961) visualized that as swelling takes place, the lamellae will move relative to one another. Some edge-to-face bonds may just slide along the surface without being broken, whilst other links may be broken and reformed. Other evidence for the existence of edge-to-face bonds was supplied by pretreating the clay suspension with polymetaphosphate which is known to neutralize the positive charges on the edges of kaolinite crystals (Cashen, 1959; Quirk, 1960). Such a pretreatment has been shown to result in an increase in the swelling of montmorillonite (van Olphen, 1950).

Montmorillonite saturated with divalent cations does not show extensive crystalline swelling, and interlamellar expansion is limited to 19 Å, even in distilled water (Norrish and Quirk, 1954). Diffuse double layer concepts are therefore not applicable to the interlamellar swelling of Ca^{++} montmorillonite since at this separation between lamellae diffuse double layers are not formed.

The limited crystalline swelling of Ca^{++} montmorillonite indicates the presence of an attractive potential barrier at a basal separation of 19 Å. The nature of this barrier is not well understood. The existence of short-range electric attractive forces at close distances of separation between lamellae (<30 Å) has been postulated by MacEwan (1948<u>b</u>,1954). It was suggested that when two opposing montmorillonite lamellae approach each other sufficiently closely (<10 Å) their Stern layer cations may coalesce and it is the interaction between the Stern layers which gives rise to an electrical attractive potential. Another factor which may contribute towards the increased attraction between lamellae of Ca^{++} montmorillonite is the increase in the radius of dielectric saturation of the calcium ion in comparison to the sodium ion.

It is also suggested that an interlamellar calcium ion is "bonded" to two opposing plates, thereby restricting the tendency of the ion to dissociate from the surface. On the other hand, a calcium ion on the external crystal surface shares its charge with two adjacent negative spots of one plate. Such an ion has a higher entropy and a greater tendency to leave the surface and take part in a diffuse double layer distribution. The results of negative adsorption studies on calcium montmorillonite suspensions by Edwards and Quirk (1962) are consistent with this view.

(ii) Intercrystalline swelling

Intercrystalline swelling is a general phenomenon common to both expanding and non-expanding lattice type clay minerals. Since much work on the mechanism of intercrystalline swelling has been carried out on illites this will be discussed in detail.

The work of Aylmore and Quirk (1960b and c) shows that for an illite saturated with monovalent cations intercrystalline swelling is determined by a potential barrier which is overcome in dilute electrolyte concentrations. A continuous increase in solution uptake at pF 1 was observed as the salt concentration was decreased as would be predicted from diffuse double layer theory. Thus in distilled water Na^{+} Willalooka illite adsorbed

8.4 cc of water per g of clay as compared to 0.48 cc/g in M NaCl solution which is of the same order of magnitude as the amount of water taken up by the Ca^{++} clay in distilled water suggesting the presence of a potential barrier for the Na^{+} illite similar to that present in montmorillonite.

The intercrystalline swelling of Ca^{++} Willalooka illite is restricted at all levels of electrolyte concentrations and is very insensitive to variations in concentration below molar. Thus at pF 1, Ca^{++} illite takes up 0.45 cc of solution per g of clay in the range from distilled water to M $CaCl_2$ and diffuse double layer concepts are clearly not applicable to this situation. The intercrystalline swelling of Ca^{++} illite can be compared to the limited crystalline swelling of Ca^{++} montmorillonite which has been shown to give a constant basal separation of 19 Å from distilled water to M $CaCl_2$ solution. However, it must be remembered that the average distance of separation between crystals in Ca^{++} Willalooka illite ($\simeq$30 Å, from pore size distribution studies) is considerably greater than the distance separating the lamellae within a crystal of Ca^{++} montmorillonite ($\simeq$10 Å). Even if electrical attractive forces of the type suggested by MacEwan (1948<u>b</u>, 1954) were operative in Ca^{++} illite, the magnitude of these forces would be very much smaller since their rate of decay with increasing interparticle distance is very steep.

It is to be expected that particle to particle interaction which results in intercrystalline swelling and the creation of a gel structure would be important in determining the solution uptake at any given hydrostatic suction. The dependence of intercrystalline swelling on the structural status of the clay system has been demonstrated by the results of Croney and

Coleman (1954), Holmes (1955) and Aylmore and Quirk (1960<u>b</u> and <u>c</u>). These workers have shown that at any given hydrostatic suction a clay mass may have a range of water contents depending on the previous history of the clay. As a clay mass is repeatedly wet and dried it may describe a series of hysteresis loops.

To account for these observations, Aylmore and Quirk (1959, 1960, <u>a</u> and <u>b</u>) have put forward the hypothesis that a clay mass is made up of groups of oriented crystals, termed domains, which are arranged in turbulent array. On wetting, pore expansion takes place as the distance between crystals making up a domain and that between individual domains increases, resulting in particle re-arrangement which gives rise to swelling and the creation of a gel structure. Condensation into domains as water is sucked out by increasing the hydrostatic suction is not reversible, resulting in a different structural arrangement from the original status. The irreversibility in the expansion-contraction process of the clay mass gives rise to differences in pore volume and to a series of hysteresis loops.

The swelling of a domain can be regarded as analogous to the interlamellar swelling of a montmorillonite crystal since in both instances a potential barrier exists which must be overcome before extensive swelling takes place. For a monovalent ion system it seems likely that once this barrier is exceeded, diffuse double layers are formed. In divalent ion systems, however, the attractive potential appears to be sufficiently great so as to prevent the expansion of the domains and intercrystalline swelling in this instance is therefore restricted and independent of the external electrolyte concentration.

The similarity between the intercrystalline swelling of illite and the interlamellar swelling of montmorillonite indicates that the mechanism by which clay surfaces adsorb water may be similar in both cases. Recent studies by Posner and Quirk (1963) on the adsorption of water from strong electrolyte solutions by illite and montmorillonite have led to the conclusion that surface adsorption of one or two layers of water provides the trigger mechanism for the formation of a gel structure. Since surface adsorption of water is a function of the exchangeable cations and the structural configuration of the surface atoms of the clay, it is not surprising that the mechanism whereby swelling is initiated is similar for both illite and montmorillonite.

I. 2. 5. Film Thickness and Negative Adsorption of Anions

The swelling (intra- and inter-crystalline) of clay minerals has also been interpreted and discussed in terms of the film thickness developed at the clay-solution interface. With montmorillonite the application of X-ray methods provides a direct estimate of the film thickness developed in the interlamellar space (Norrish, 1954).

In its simplest form the film thickness retained by a clay surface is experimentally determined by dividing the water content at any given hydrostatic suction by the total surface area of the clay. The experimentally derived value can then be compared to the theoretical film thickness obtained by applying the Schofield equation (1946) to the experimental conditions. This equation is written as

$$X = \frac{2}{v\sqrt{\beta c_o}} \cdot \cot^{-1} \frac{2\sqrt{c_o}}{6\sqrt{\beta}} \qquad \ldots\ldots(19)$$

where X is the film thickness adhering to a single planar charged surface of surface density of charge σ ; v is the valency of the counter ion; c_o is the concentration of the external electrolyte solution and β is a constant dependent on temperature and the dielectric constant of the medium.

It has been pointed out by Aylmore and Quirk (1960<u>b</u>) that before comparisons between theoretical and experimentally determined values for film thickness could be made, the water which is directly associated with the clay surface must be differentiated from that which is part of the gel structure. Calculated values of film thickness for cores of Ca^{++} montmorillonite at different hydrostatic suctions after correcting for interlamellar water, deviated significantly from those calculated by applying equation (19). Similar results were obtained with Na^{+} montmorillonite cores. These results illustrate the importance of structural arrangement on the quantity of water retained by clay surfaces.

Negative adsorption measurements provide an alternative estimate of the importance of diffuse double layers at clay surfaces. The deficit of anions in the vicinity of a negatively charged clay surface can be expressed by the equation derived by Schofield (1947) from diffuse double layer theory

$$\frac{\Gamma_-}{n} = \frac{q}{\sqrt{v\beta n}} - \frac{4}{v\beta\sigma} \qquad \ldots\ldots(20)$$

where Γ_- is the negative adsorption of anions per unit area and n is the normality of the external solution. The ratio Γ_-/n has therefore the dimension of length; q is a factor depending on the valency ratio of attracted and repelled ions.

For Na^+ montmorillonite, values of film thickness calculated from equation (19) are about 2/3 of the negative adsorption depth ($q/\sqrt{v\beta n}$) indicating that diffuse double layer concepts are applicable to this situation. The full development of diffuse double layers over the entire clay surface was not achieved, however, since the surface area calculated from equation (20) was only 560 m^2/g as compared to the theoretical figure of 760 m^2/g for montmorillonite. The results obtained for Ca^{++} montmorillonite indicate that diffuse double layers are formed on the external crystal surfaces when the crystals are in suspension (Edwards and Quirk, 1962).

I. 3. Adsorption of Organic Compounds by Clays

I. 3. 1. Organic Cations

The cations associated with the negatively charged clay surface can enter into exchange reactions with other organic cations in the external solution. The general principles of ion-exchange mechanisms have been established from detailed studies on synthetic resins and clays (Helfferich, 1962; Grim, 1953).

These principles may be summarized as follows:

(i) Ion-exchange reactions are in general stoichiometric and reversible.

(ii) The cation of higher valency is adsorbed in preference to that of lower charge.

(iii) The cation with the smaller hydrated equivalent volume is preferred.

(iv) Only a portion of the adsorbed cations is likely to be dissociated from the surface, this percentage being dependent on the nature of the clay and the cation, the water content and the relative concentration of the cation.

(v) A single cation species may be adsorbed at the clay surface with different energies.

The above principles are also applicable to ion-exchange reactions involving organic cations. In addition, the following facts have been established:

(i) The replacement of the inorganic cations originally present at the clay surface by large organic cations may not proceed to completion. This effect is referred to as the "cover-up" effect (Hendricks,1941).

(ii) In addition to electrostatic forces, van der Waals or physical adsorption forces can be important in the adsorption of organic cations by clays. With large cations, the latter may become appreciable and adsorption in excess of the cation exchange capacity of the clay has been observed (Grim, Allaway, and Cuthbert, 1947; Cowan and White, 1958; Greenland and Quirk, 1960).

(iii) The adsorption of some organic solutes over and above the exchange capacity appears to take place as ion pairs, that is, the adsorption of anions accompanies that of the cations (Greenland and Quirk, 1960).

(iv) The adsorption of organic cations by montmorillonite in the interlamellar space increases the basal spacing and hence the volume of the clay system, by propping apart the lamellae of the crystals. (Barrer and MacLeod, 1955; Barrer and Reay, 1957).

(v) The organic clays frequently lose their original hydrophilic and swelling properties in water and show organophilic characteristics (Jordan, 1949; Weiss, 1963).

I. 3. 2. Organic Polymers

This review on adsorption of organic polymers by clays is confined to uncharged, linear macromolecules. The mechanism of polymer adsorption from solutions onto solid adsorbents has been reviewed and discussed in detail by Silberberg (1962b). The main features are:

(i) The adsorption increases with increasing molecular weight up to a certain limiting size.

(ii) The polymer is adsorbed with a large fraction of its segments attached to the adsorbent surface with short loops of unattached segments extending away from the surface.

(iii) The dependence of the adsorption on temperature is small and the change in energy involved to cause the polymer chain to collapse onto the surface is only in the order of a few kT per surface - segment contact.

(iv) The adsorption process is practically irreversible.

I. 3. 3. Theoretical Considerations of the Adsorption Process

(i) Adsorption of organic cations by an ion-exchange mechanism

Ion-exchange equilibria can be characterized by the ion-exchange isotherm which graphically represents the ionic composition of the ion exchanger, in this instance the clay material, under a given set of experimental conditions and at a particular temperature.

Ion-exchange equilibria may also be described in terms of the selectivity coefficient, K_s, which is defined by the general relationship,

$$K_s = \frac{N_A^{v_B} . C_B^{v_A}}{N_B^{v_A} . C_A^{v_B}} \qquad \text{......(21)}$$

where N_A and C_A are the molal concentration of the ionic species A in the clay and in solution, respectively. N_B and C_B refer to the same quantities for species B; v_A and v_B are the valencies of A and B, respectively. Molarities or equivalent ionic fractions have been used instead of molalities.

An equation similar to (21) can also be derived by applying the mass-action law (neglecting activity coefficients) to the heterogeneous system of clay and solution. For the exchange reaction involving two monovalent cations, A^+ and B^+, one can write

$$A^+ + B\text{-}Z \rightleftharpoons B^+ + A\text{-}Z \qquad \ldots\ldots(22)$$

where Z refers to the clay phase.

The mass action coefficient, K_m, is then given by

$$K_m = \frac{N_{A-Z}.C_{B^+}}{N_{B-Z}.C_{A^+}} \qquad \ldots\ldots(23)$$

where the symbols refer to identical quantities as for equation (21).

In theoretical discussion it is customary to use the thermodynamic equilibrium constant, K_a, which is defined as

$$K_a = \frac{a_{A-Z}\cdot a_{B^+}}{a_{B-Z}\cdot a_{A^+}} \qquad \ldots\ldots(24)$$

where a_{A-Z} and a_{B-Z} refer to the activities of A^+ and B^+ on the clay phase and a_{A^+} and a_{B^+} to those in solution, at equilibrium. Before equation (24) can be applied to the experimental data, it is required that the activity coefficients of A^+ and B^+ both in the clay and in the solution phase, be known. Activity coefficients of electrolytes in aqueous solution are readily available but the corresponding quantities for the clay phase cannot be estimated without assumptions (Kerr, 1928; Boyd, Schubert and Adamson, 1947).

By means of rigorous thermodynamics, activity coefficients can only be obtained from measurements of those equilibrium systems to which they are to be applied (Gaines and Thomas, 1953).

The activity coefficient for mono-, di-, and trimethylammonium chloride in aqueous solution at 25°C have been determined by Whitlow and Felsing (1944) and those for tetraalkylammonium salts have been compared and discussed by Stokes (1963). The lack of precise experimental data on the activity coefficients of other alkylammonium salts makes it difficult for exact thermo-dynamic calculations to be carried out in the present instance.

If the ratios of the activity coefficients in the clay and in the solution phase are assumed to remain constant at each equilibrium point of the isotherm, equation (23) can be written as

$$K_a = \frac{N_{A-Z.}\ C_{B^+}}{N_{B-Z.}\ C_{A^+}} \cdot K_f \qquad \text{......(25)}$$

$$= K_m \cdot K_f \qquad \text{......(26)}$$

Where K_f refers to the quotient of activity coefficients in both phases. The standard free energy change for the ion-exchange reaction is then given by

$$-\Delta G^o = RT \ln K_a \qquad \text{......(27)}$$

$$= RT \ln K_m + RT \ln K_f \qquad \text{......(28)}$$

$$= -\Delta G^m + \text{constant, for constant } K_f \qquad \text{......(29)}$$

In the exchange adsorption of a monovalent cation by a divalent cation-clay system, the exchange equilibrium may be represented as

$$2A^{+} + B - Z \rightleftarrows 2(A - Z) + B^{++} \qquad ......(30)$$

and the corresponding expression for K_a is

$$K_a = \frac{N^2_{A-Z} \cdot C_{B^{++}}}{N_{B-Z} \cdot C^2_{A^+}} \; K_f \qquad ......(31)$$

$$= K_m \cdot K_f \qquad ......(32)$$

In so far as K_f is constant, K_m will be constant.

Cowan and White (1958) have applied the mass-action treatment to the exchange adsorption equilibrium between Na^+ montmorillonite and a homologous series of n-alkylammonium cations in aqueous solution. They have obtained a linear relationship between the free energy change (ΔG^m) and the number of carbon atoms of the alkyl chain for these compounds. However, determinations of K_m and ΔG^m are only valuable for purposes of comparison under a given set of experimental conditions. Values of K_m and ΔG^m are dependent on the conditions under which the experiment is carried out as opposed to the thermodynamic equilibrium constant (K_a) which is a true constant and only dependent on temperature.

Another approach to the treatment of ion-exchange adsorption equilibria is to treat the exchange process as a simultaneous competition of two cations, A^+ and B^+ for the adsorbent surface (Langmuir, 1916; Boyd, Schubert and Adamson, 1947). The adsorption of A^+ ions from a dilute solution is given by

$$(x/m)_A = \frac{kb_1 \, C_{A^+}}{1 + b_1C_{A^+} + b_2C_{B^+}} \qquad ......(33)$$

where $(x/m)_A$ refers to the amount of A^+ ions adsorbed per unit weight of adsorbent (clay); k_1, b_1, and b_2 are empirical constants. For the case where b_1C_A+ and $b_2C_B+ \gg 1$, the quantity unity in equation (33) can be neglected. Writing N_{A-Z} for $(x/m)_A$ and rearranging terms, equation (33) can be written in the linear form as

$$\frac{C_A+ \;/ \;C_B+}{N_{A-Z}} = \frac{b_2}{b_1k} + \frac{1}{k} \;.\; C_A+ \;/\; C_B+ \qquad \text{......(34)}$$

A straight line is obtained when the left hand term is plotted against the ratio of $C_A+ \;/\; C_B+$.

For small values of C_A+ as compared to C_B+, the amount of A^+ ions adsorbed would be proportional to C_A+ . This relationship is represented by the initial slope of the "Langmuir-type" isotherm which is more or less linear for small values of C_A+ . On the other hand, equation (34) predicts that when $C_A+ \gg C_B+$, the term N_{A-Z} becomes independent of C_A+, provided that no physical adsorption takes place and interaction between adsorbed cations is not significant. At high surface coverages and when the cations involved are large, interaction between sorbate molecules at the surface may become important and under these conditions this relationship would not be expected to hold true.

For the case where a monovalent cation, A^+, is adsorbed by a divalent (B^{++}) ion-clay system, the corresponding equations are

$$N_{A-Z} = \frac{kb_1 \; C^2_{A+}}{b_1C^2_{A+} + b_2C_{B}++} \qquad \text{......(35)}$$

or in the linear form as

$$\frac{C_{A^+}^2 / C_{B^{++}}}{N_{A-Z}} = \frac{b_2}{b_1 k} + \frac{1}{k} \cdot C_{A^+}^2 / C_{B^{++}} \qquad \ldots\ldots(36)$$

(ii) Adsorption of uncharged linear flexible polymers

The theory of the adsorption of uncharged flexible macromolecules onto solid surfaces has been considered in detail by Silberberg (1962*a* and *b*). This theory appears to satisfy most of the observed experimental facts of previous workers.

Unlike the Frisch-Simha-Eirich theory (1953, *a* and *b*), which predicts a rather small fraction of segments on the surface, this approach results in a substantial fraction of the segments being on the surface, even at low interaction energies. Adsorption reaches a plateau which is molecular weight dependent; adsorption increasing with increasing molecular weight, but at a decreasing rate, becoming independent when it is very high. It is shown that the temperature dependence of adsorption is small and no further large increase in adsorption would occur beyond a value of 2kT for the energy of adsorption per segment of polymer.

The theory predicts that the polymer molecules are practically flattened into the surface and that the shape of the adsorbed polymer molecule is largely independent of molecular weight and concentration.

I. 4. Measurement of Crystalline Swelling of Clay-Organic Complexes and Orientation of Adsorbed Molecules

The crystalline swelling of montmorillonite saturated with inorganic cations has been studied in some detail by X-ray diffraction techniques (Hendricks, Nelson, and Alexander, 1940; Mooney, Keenan, and Wood, 1952b; Norrish, 1954). The general conclusions have been considered in I. 2. and can be summarized as follows:

(i) Crystalline swelling proceeds in a step-wise manner up to a few layers of water, and is limited to an interlamellar separation of about 20 Å.

(ii) Crystalline swelling is primarily determined by the nature and the hydration energy of the interlamellar cations and the surface charge density of the clay.

(iii) With a few monovalent cations, the hydration energy is such that the potential barrier at 20 Å is overcome and diffuse double layers are developed resulting in a large increase in the volume of the clay-water system.

Comparable experimental data on the crystalline swelling of clay-organic complexes are lacking. Since crystalline swelling is influenced by surface-cation forces it is to be expected that the progressive replacement of the inorganic cations by organic ions would modify the hydration and swelling behaviour of the clay system. It is known that the amount of water adsorbed is reduced as increasing numbers of exchange sites become occupied by organic cations (Hendricks, 1941; Kurilenko and Mikhalyuk, 1958). This reduction has been attributed to the decrease in surface available for sorption of water molecules and to the increase in the hydrophobic character of the clay material.

Diamond and Kinter (1961) have studied the interlamellar separations of montmorillonite saturated with short-chain mono-, di-, tri-, and tetraalkylammonium cations both in the moist and in the oven-dry condition. For cations containing less than five carbon atoms the basal spacing for the moist complexes may be greater by a value of 0.3 - 0.7 Å than for the oven-dry specimens. This variation was attributed to the entry of water molecules into the interlamellar space. When the alkyl chain exceeded six carbon atoms, differences in the interlamellar separation between the moist and oven-dry specimens of the complexes did not exceed 0.1 Å.

It has been shown by Weiss (1963) that the crystalline swelling of complexes between n-alkylammonium ions and different mica-type layer silicates was dependent on the length of the alkyl chain and the surface density of charge of the silicate mineral. The basal spacing in water of montmorillonite complexes remained virtually unchanged at 13-14 Å from the ethyl- to the n-decylammonium derivatives. The first large increase in the interlamellar separation was only observed with the n-dodecylammonium complex. Similar results have been obtained by Greene-Kelly (1956) and Jordan (1949).

Results of X-ray diffraction measurements on complexes between montmorillonite and organic compounds have frequently been discussed in terms of the difference between the observed d(001) spacing of the complex and the thickness, t, of the montmorillonite lamella (Figure 1b). It has been commonly observed by many workers that Δ-values for a number of complexes were less than the minimum molecular thickness of the adsorbed molecules (MacEwan, 1948a; Talibudeen, 1955; Barrer and Reay, 1957; Hoffmann and Brindley, 1960; Greenland, Laby, and Quirk, 1962). The observed contraction in the van der Waals thickness of the adsorbed molecules has been attributed to some specific bonding mechanism, such as C-H ... O hydrogen bonding between the methylene groups of the molecule and the oxygen atoms of the silicate surface (Bradley, 1945; MacEwan, 1948a) or to the interaction of delocalized π electrons of planar aromatic compounds with the clay surface (Haxaire and Bloch, 1956). Alternatively, the observed contraction is thought to arise from the fact that the adsorbed molecules may become embedded or "keyed" into the hexagonal depressions of the silicate surface (Greenland, Laby, and Quirk, 1962; Rowland and Weiss, 1961).

X-ray diffraction techniques have also been used to obtain information of the orientation of the adsorbed molecules in the interlamellar space. As a general rule it can be stated that as a consequence of the additivity of van der Waals forces, polyatomic molecules tend to lie flat on the adsorbent surface. This tendency is opposed by the anisotropy of polarizability of the molecule which would tend to orient it with its axis of greatest polarizability perpendicular to the surface. Additivity frequently outweighs the effect of anisotropy (de Boer, 1936, 1950).

It has been shown that at low surface coverage the organic molecules tend to be adsorbed in such a manner as to present their minimum thickness thus providing maximum van der Waals contact with the surface of the clay (Hendricks, 1941). At high surface coverage, the molecules may reorient themselves so as to allow a closer packing of adsorbed molecules at the surface (Greenland and Quirk, 1960 ; Rowland and Weiss, 1961).

I. 5. Modification of the Swelling Properties of Clays and Soils by Adsorption of Organic Compounds.

I. 5. 1. Organic Cations

In the search for materials which may improve the water-stability and aggregation of soils, a number of quaternary nitrogenous compounds with long hydrocarbon chains have been found to be effective. Their effectiveness appears to be related to the ability of these compounds to control the rate of wetting and reduce the swelling of the soil. The addition of small amounts of cetylpyridinium bromide in solution to a clay loam resulted in a marked reduction of the swelling of this material (Clare, 1947). Treating a silt loam with 1 per cent dimethyldioctadecylammonium chloride has also been found to increase the water-stability and the ability to withstand break-down by cyclic wetting and drying of the soil (Grossi and Woolsey, 1955). Emerson (1962) has presented evidence that the addition of 1 per cent cetyltrimethylammonium bromide (CTAB) to Ca^{++} montmorillonite prevented large intercrystalline swelling of this material in water and dilute $CaCl_2$ solutions.

The mechanism by which adsorbed organic cations may stabilize soil and clay materials and reduce the swelling ability of such materials is thought to be due to the modification of the particle-particle interaction. It has been shown that appreciable energies (1-4kT) are involved in the adsorption of organic cations by clays (Cowan and White, 1958; Greenland, Laby and Quirk, 1962). The tendency of the adsorbed molecules to dissociate from the clay surface to form diffuse double layers when placed in water will be reduced as a consequence. In addition the hydrocarbon part of the molecule renders the clay more hydrophobic and disrupts the water structure at the clay surface.

The interlamellar swelling of complexes between montmorillonite and n-alkylammonium cations has been studied by Weiss (1963) and his results have been discussed in the previous section.

The swelling of complexes between vermiculite and n-alkylammonium cations was different from that of the corresponding montmorillonite complexes (Walker, 1960; Garrett and Walker, 1960). Vermiculite complexes with n-propyl-, n-butyl-, and isoamylammonium ions swelled considerably when put in water giving rise to large interlamellar separations. It was thought that swelling was initiated by the formation of ordered water structures around the cations. Water molecules were thought to act as host to the alkylammonium cations which supported the water. Such an association between water and cation resembles the "ice-berg" structure of Frank and Evans (1945) and may be referred to as an inclusion complex or a clathrate compound in which molecules of one substance (alkylammonium ions) are contained within the framework of the other (water molecules). This suggestion was supported by the observation that the unswollen butylammonium complex did not swell when placed in water at 50°C. However, the interlamellar expansion of this complex in solutions of butylammonium salt of different concentrations (C) was a linear function of $C^{-\frac{1}{2}}$, indicating that the cations were distributed in a diffuse double layer. This observation is rather difficult to reconcile with the ordered framework of water molecules required for the formation of a clathrate compound. Furthermore, complexes with methyl-, ethyl-, and higher members of the homologous series of n-alkylammonium cations did not show extensive swelling in water. No satisfactory explanation has been put forward to account for the observed difference between these and the butylammonium complexes.

I. 5. 2. Organic Polymers

It is known that the stability of natural soil aggregates is related to the presence of polymeric substances in the soil. Of these substances, the polysaccharides, which have been shown to occur in soils (Forsyth, 1947; Chesters, Attoe, and Allen, 1957; Lynch, Olney, and Wright, 1958) have received considerable attention. It has been shown that bacterial polysaccharides when added to soil increased aggregation (Geoghegan and Brian, 1948; Martin, 1945) and that aggregate stability was markedly reduced by periodate treatment which appeared to be specific to removal of polysaccharides (Greenland, Lindstrom, and Quirk, 1962). Considerable attention has also been given to the manner in which synthetic organic polymers and polyelectrolytes may improve aggregation and the water-stability of natural soil aggregates (Hedrick and Mowry, 1952; Hagin and Bodman, 1954; Ruehrwein and Ward, 1952; Emerson, 1956; Williams, 1959).

The manner in which synthetic polymers stabilize soil aggregates is thought to be by interparticle bonding whereby a polymer molecule is attached to several soil or clay particles. In addition to interparticle bonding the polymer molecule when introduced into an already aggregated system may spread over adjacent soil or clay surfaces thereby strengthening the pores within an aggregate. This mechanism is thought to be responsible for the stability of virgin aggregates as compared to those of cultivated ones (Panabokke and Quirk, 1957). In virgin aggregates, the water moves in a controlled fashion from the coarse pores to the remainder of the pore space and disruption of the aggregate by differential swelling is prevented. The lack of organic strengthening materials in cultivated aggregates predisposes the aggregates to fail when wet rapidly (incipient failure) due to the creation of planes of failure along which water can move rapidly.

The introduction of an uncharged linear flexible polymer, such as polyvinyl alcohol, into the pores of a natural soil aggregate has been shown to increase the water-stability and mechanical strength of the aggregate. The rate of wetting was controlled but the equilibrium water content may not be appreciably different from that of the untreated aggregate (Williams, 1959).

If the water uptake and swelling of clay-polymer complexes are controlled by the degree of interparticle bonding between clay and polymer, these properties would be similar to those shown by cross-linked ion-exchange resins. The uptake of water at high values of relative humidity by an ion-exchange resin was dependent on the swelling pressure, and for equal water contents, this pressure was higher in resins with the higher degree of cross-linking (Boyd and Soldano, 1953). The ability of the resin to swell was also reduced as the degree of cross-linking was increased (Gregor, Gutoff, and Bregman, 1951; Pepper, Reichenberg, and Hale, 1952). The reduction in swelling was attributed to the increase in the rigidity of the resin as the number of cross-links in the network increased.

CHAPTER II.

THE FORMATION OF COMPLEXES BETWEEN MONTMORILLONITE AND ALKYLAMMONIUM COMPOUNDS

II. 1. Introduction

The replacement of the exchangeable cations by adsorption of organic compounds is expected to modify the surface adsorption of water which is thought to be the trigger mechanism for particle re-arrangement giving rise to swelling and the creation of a gel structure. For this reason the mechanism whereby organic cations are adsorbed by the clay must be fully understood. The adsorption of an homologous series of alkyl -substituted ammonium compounds by montmorillonite has therefore been studied in some detail. Previous work by Cowan and White (1958) and Greenland, Laby and Quirk (1962) has illustrated the advantage of using an homologous series of organic compounds. In addition, the structure of the compounds used in the present work is well known and the orientation and conformation of the adsorbed molecules can be studied by X-ray diffraction and infra-red spectroscopy methods.

II. 2. Experimental

II. 2. 1. Materials

a. The clay material

The montmorillonite used was supplied by the Fuller's Earth Company, Redhill, Surrey, England. The material as received, was predominantly calcium saturated containing about 3 per cent free carbonate. In order to prepare a dispersed suspension from which the clay fraction could be separated, it was necessary to replace the calcium originally present by sodium ions. This was achieved by repeated washing with N NaCl solution followed with distilled water. A 2 per cent aqueous suspension was prepared from the sodium saturated material and the $<2\mu$ equivalent spherical diameter was separated by sedimentation under gravity and decantation, repeating the process twice. Removal of carbonate impurities was also necessary since this material may possess surface-active properties. To remove the carbonate the clay suspension was allowed to react with a calculated amount of HCl (added in a solution of N NaCl) for about 10 minutes with vigorous stirring. Aluminium present as surface impurities was removed by washing the clay fraction with N NaCl adjusted to pH 3 with HCl, centrifuging and decanting the supernatant liquid. This process was repeated five times, followed by several washings with N NaCl at approximately pH 5.8 and finally with distilled water. Complete removal of aluminium was probably not achieved due to the migration of lattice-bound aluminium to the exchange sites as surface aluminium dissociates into solution under acid conditions (Bolt and Warkentin, 1956; Lin and Coleman, 1960). Excess electrolyte was removed by dialysing the clay suspension contained in "Visking" cellulose casings against distilled water, renewing the water every 24 hours. Dialysis was terminated when the water reached an equilibrium resistance of $0.25 \times 10^6 \Omega$ (approximately after a period of 15 days). The dialysed material was dried in an electric oven at 70°C, ground in a mortar and passed through a 60 mesh sieve. To obtain the calcium form, the sodium clay suspension was flocculated by adding solid $CaCl_2$, followed by repeated washing with N $CaCl_2$ solution and then dialysed as previously described.

The exchange capacity of the sodium and calcium clay material was determined by two methods, details of which are presented in Appendix I.

b. The organic compounds

The sources of supply, structural formulae and purity checks of the compounds used are presented in Appendix II.

II. 2. 2. Methods

a. The preparation of alkylammonium-montmorillonite complexes

The complexes between montmorillonite and alkylammonium compounds were prepared by adding a known volume of standard solutions of the alkylammonium salt of varying strength to an accurately weighed quantity of the air-dry clay powder contained in stoppered polythene bottles. In a preliminary investigation it was shown that no further increase in the amount of organic compound adsorbed occurred after shaking the contents for 2 hours on the end-over-end mechanical shaker. An overnight shaking was adopted in all instances to ensure that equilibrium was attained. For this purpose the bottles containing the clay and alkylammonium solution were placed on the shaker in a constant temperature room, maintained at 25°C. The suspension was centrifuged at 3,500 r.p.m. in the M.S.E. centrifuge or in some instances at 16,000 r.p.m. in the Lourdes high-speed centrifuge.

b. Estimation of the cations in the supernatant solution

Ammonium and the mono-, di-, and trialkylammonium ions in solution were estimated by steam distillation of aliquots with excess 40 per cent NaOH in a Markham still. The quaternary ammonium derivatives were digested according to a slightly modified Kjeldahl procedure prior to steam distillation. The inorganic ions in solution (sodium, potassium, cesium, calcium) were determined by standard quantitative methods.

Details of the methods used in the quantitative estimation of the organic and inorganic cations in the supernatant solution are presented in Appendix III.

c. Estimation of the amount of cations adsorbed

The amount of a given cation adsorbed by the clay under the conditions of the experiment was obtained by difference between the quantity initially added and that observed after equilibrium had been attained. The amount adsorbed is expressed as milliequivalents (me) per 100 g of oven-dry (105°C, overnight) clay.

d. Effect of oven-drying on the retention of adsorbed cations

It was thought that oven-drying might decompose the alkylammonium cation at the clay surface according to the following reaction

$$RNH_3\text{-clay} \longrightarrow H\text{-clay} + RNH_2$$

where R represents an alkyl group and RNH_2 represents the free amine which would have been lost in the vapour phase if the reaction took place. To investigate this point the centrifuged calcium clay containing about 45 and 65 me monomethylammonium cations per 100 g clay was dried in the oven at 70°C for 24 and 48 hours. Portions of the oven-dry complexes were analysed for amine nitrogen by steam distillation with excess 40 per cent NaOH (see Appendix III). The amount of amine liberated was identical with the amount adsorbed as calculated by method (c).

II. 2. 3. Results

The results of the adsorption experiments are presented in the form of adsorption isotherms at 25°C, in which the concentration of solute in equilibrium with the clay is plotted against the amount of solute adsorbed by the clay.

Adsorption isotherms for sodium montmorillonite are shown in Figures 2 to 5, and those for calcium montmorillonite in Figures 6 to 9.

Details of the adsorption isotherms of alkyl-substituted ammonium compounds studied are presented in Table 2.

TABLE 2.

Summary of the adsorption isotherms at 25°C as shown in Figures 2 to 9.

Cation	Notation	Montmorillonite
monomethylammonium	$Me_1NH_3^+$	sodium and calcium
monoethylammonium	$Et_1NH_3^+$	"
mono-n-propylammonium	$Pr_1NH_3^+$	"
mono-n-butylammonium	$Bu_1NH_3^+$	"
dimethylammonium	$Me_2NH_2^+$	"
diethylammonium	$Et_2NH_2^+$	"
di-n-butylammonium	$Bu_2NH_2^+$	"
trimethylammonium	Me_3NH^+	"
triethylammonium	Et_3NH^+	"
tetramethylammonium	Me_4N^+	"
tetraethylammonium	Et_4N^+	"
tetra-n-propylammonium	Pr_4N^+	sodium
tetra-n-butylammonium	Bu_4N^+	sodium and calcium
sodium	Na^+	calcium
potassium	K^+	"
ammonium	NH_4^+	"
cesium	Cs^+	"

Figure 2.

Adsorption isotherms at 25 °C of methyl-substituted ammonium cations on Na^+ montmorillonite.

In this and subsequent figures (Figures 2 to 9) the equilibrium concentration is expressed as milliequivalents per 100 ml (me %) x 50 so that the values on the abscissa correspond to the number of milliequivalents of alkylammonium cations per 100 gram of clay.

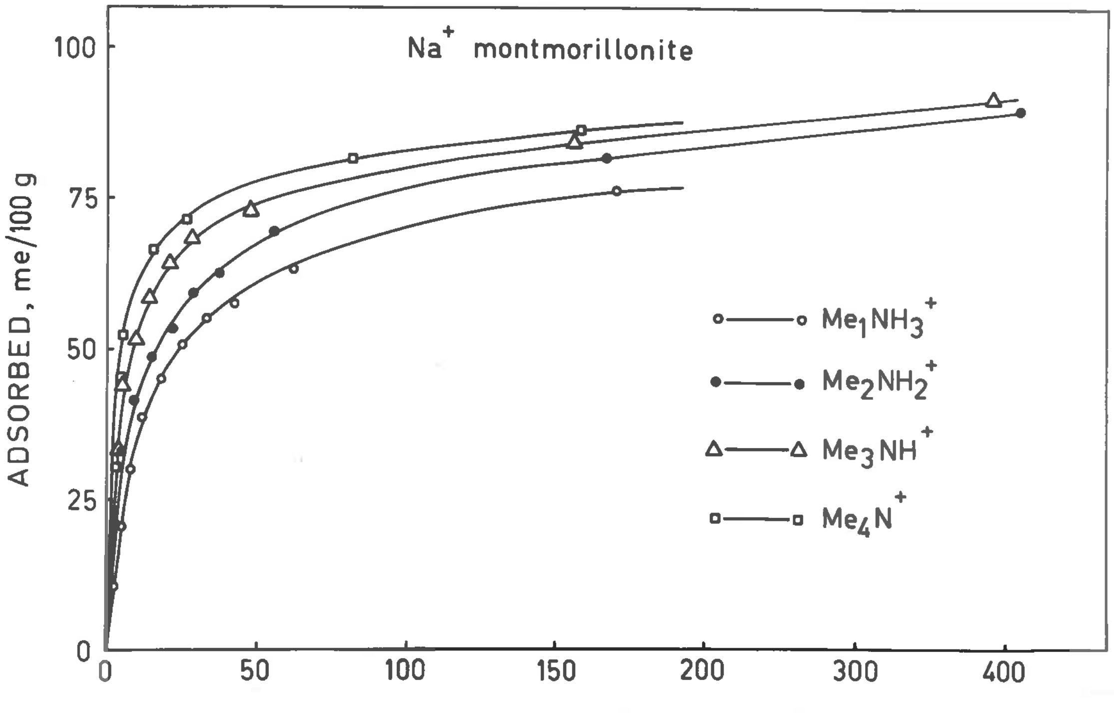

Na$^+$ montmorillonite
ADSORBED, me/100 g
0
25
50
75
100
0
50
100
150
200
300
400
EQUIL. CONC., me % x 50
Me$_1$NH$_3^+$
Me$_2$NH$_2^+$
Me$_3$NH$^+$
Me$_4$N$^+$

Figure 2

Figure 3.

Adsorption isotherms at 25 °C of ethyl-substituted ammonium cations on Na^+ montmorillonite.

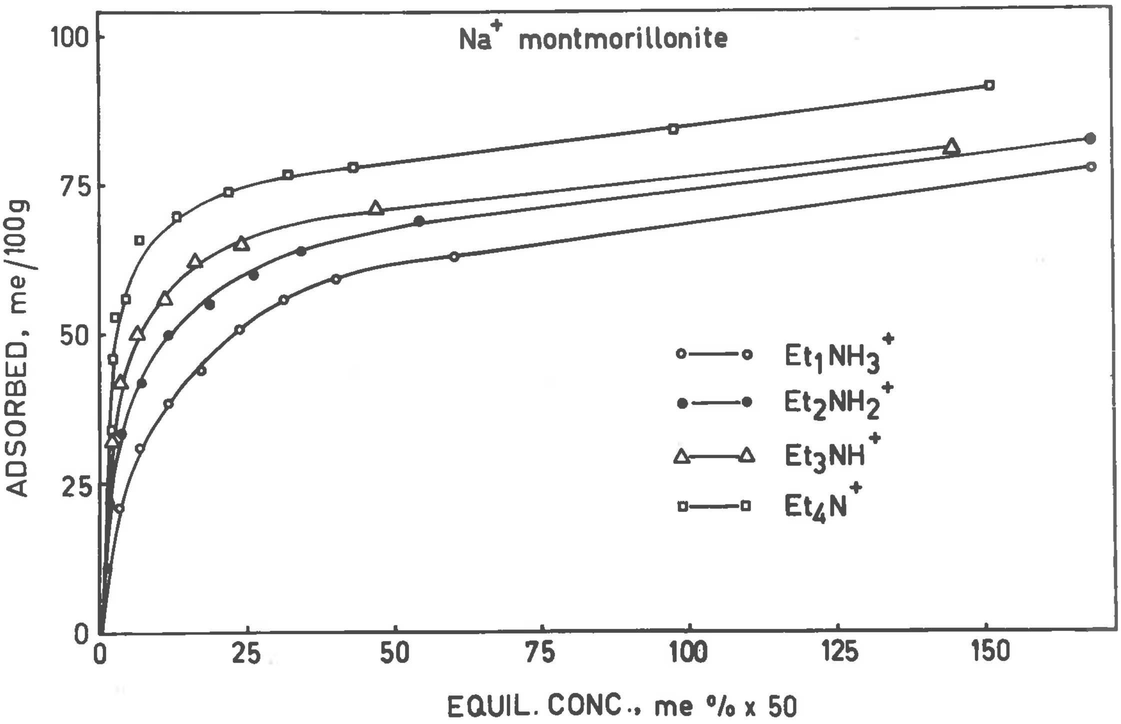

Na+ montmorillonite
ADSORBED, me/100g
EQUIL. CONC., me % x 50
0
25
50
75
100
125
150
Et1NH3+
Et2NH2+
Et3NH+
Et4N+

Figure 3

Figure 4.

Adsorption isotherms at 25 °C of propyl-substituted ammonium cations on Na^+ montmorillonite.

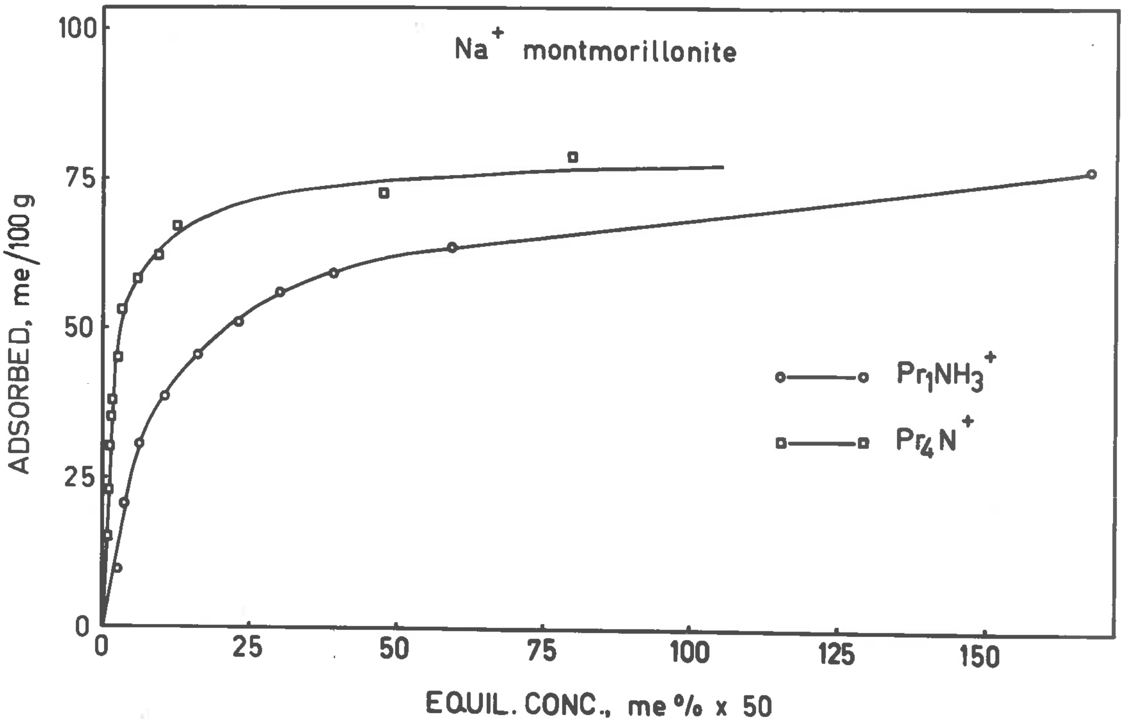

Na$^+$ montmorillonite
ADSORBED, me/100 g
EQUIL. CONC., me % x 50
0
25
50
75
100
0
25
50
75
100
125
150
Pr$_1$NH$_3^+$
Pr$_4$N$^+$

Figure 4

Figure 5.

Adsorption isotherms at 25 °C of butyl-substituted ammonium cations on Na^+ montmorillonite.

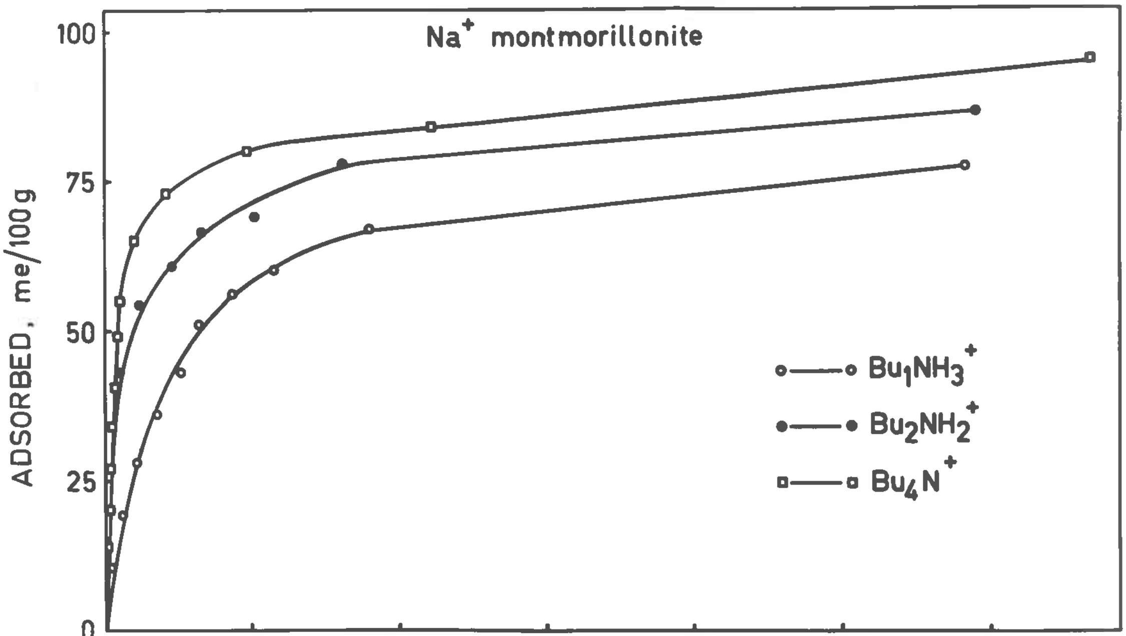

Na$^+$ montmorillonite
ADSORBED, me/100 g
EQUIL. CONC., me %x 50
0
25
50
75
100
125
150
Bu$_1$NH$_3^+$
Bu$_2$NH$_2^+$
Bu$_4$N$^+$

Figure 5

Figure 6.

Adsorption isotherms at 25 °C of methyl-substituted ammonium cations on Ca^{++} montmorillonite.

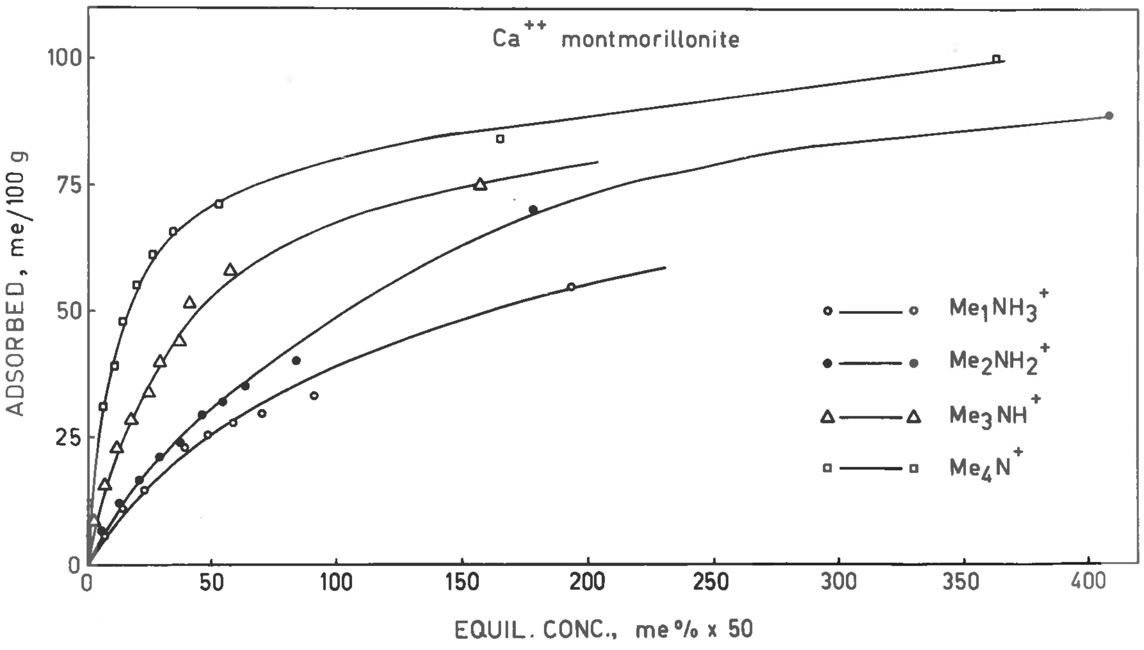

Ca^{++} montmorillonite
ADSORBED, me/100 g
EQUIL. CONC., me% x 50
0
25
50
75
100
0
50
100
150
200
250
300
350
400
Me$_1$NH$_3^+$
Me$_2$NH$_2^+$
Me$_3$NH$^+$
Me$_4$N$^+$

Figure 6

Figure 7.

Adsorption isotherms at 25 °C of ethyl-substituted ammonium cations on Ca^{++} montmorillonite.

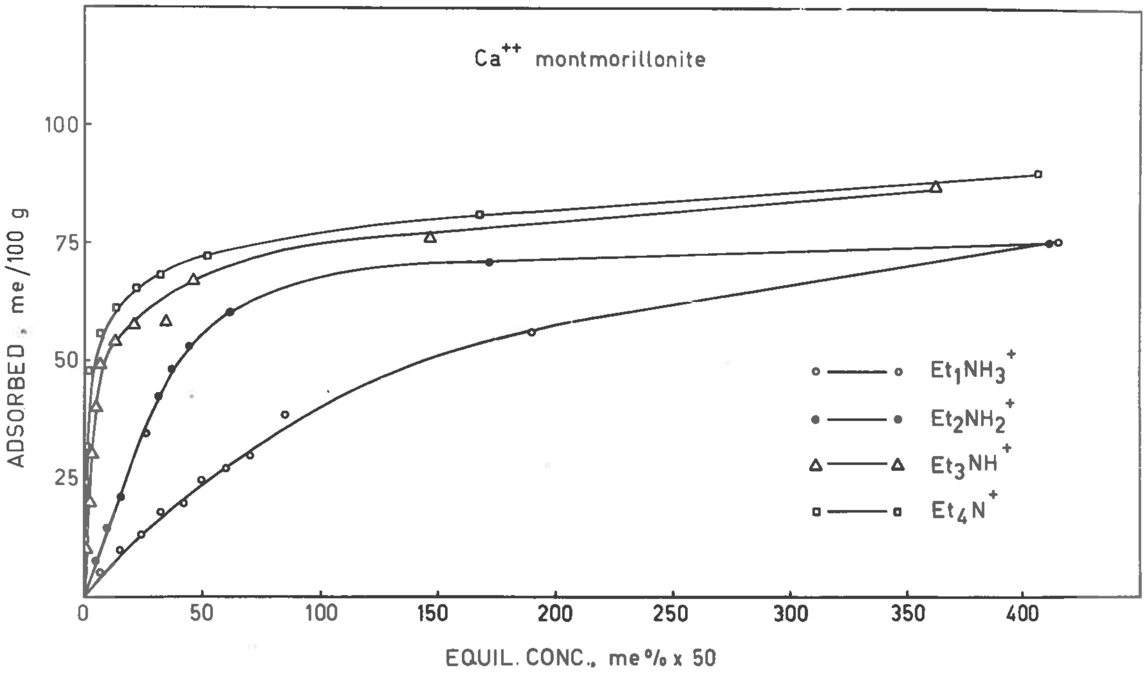

Ca^{++} montmorillonite
ADSORBED, me/100 g
100
75
50
25
0
50
100
150
200
250
300
350
400
EQUIL. CONC., me% x 50
Et$_1$NH$_3^+$
Et$_2$NH$_2^+$
Et$_3$NH$^+$
Et$_4$N$^+$

Figure 7

Figure 8.

Adsorption isotherms at 25 ^{o}C of mono-n-propylammonium and butyl-subtituted ammonium cations on Ca^{++} montmorillonite.

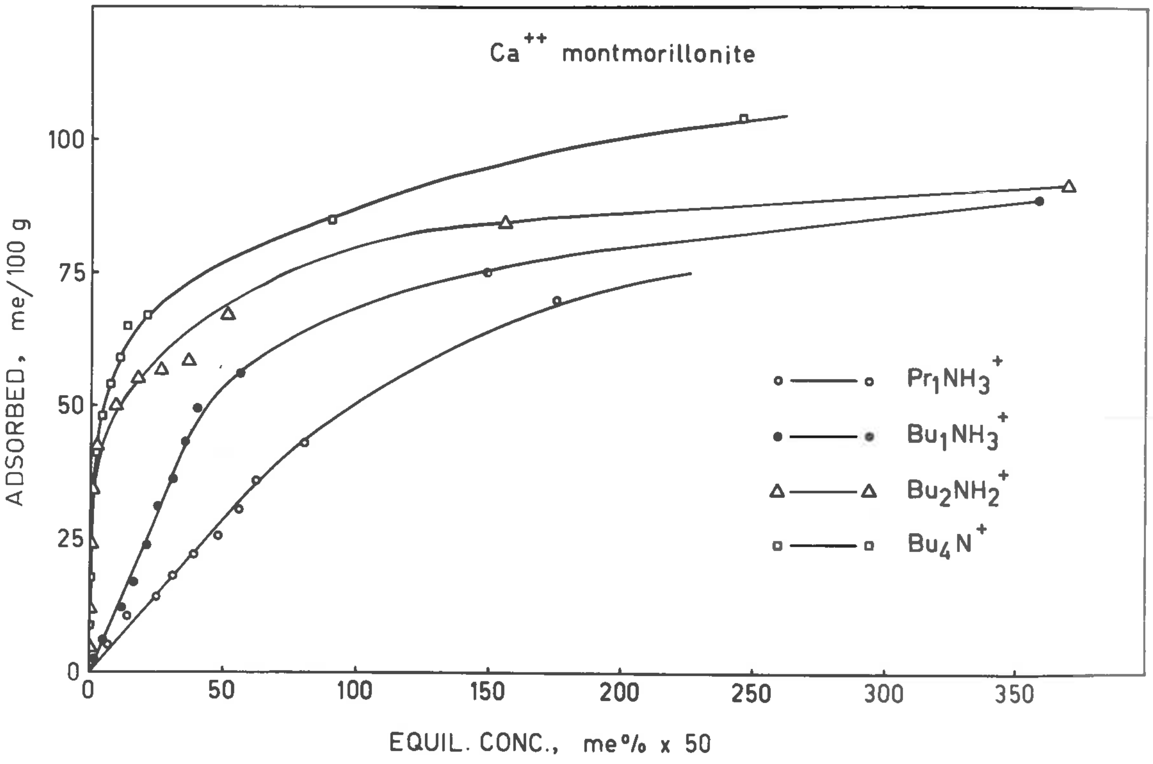

Ca++ montmorillonite
ADSORBED, me/100 g
0
25
50
75
100
EQUIL. CONC., me% x 50
0
50
100
150
200
250
300
350
Pr1NH3+
Bu1NH3+
Bu2NH2+
Bu4N+

Figure 8

Figure 9.

Adsorption isotherms at 25 °C of sodium, potassium, ammonium, and cesium ions on Ca^{++} montmorillonite.

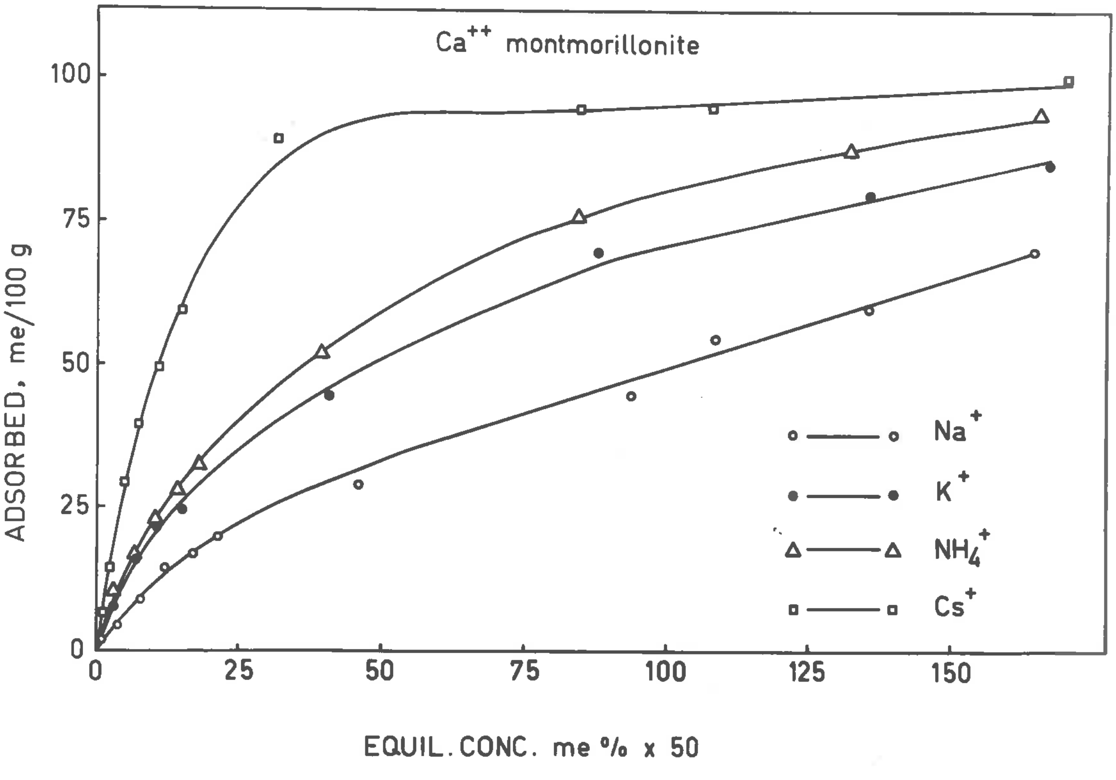

Ca^{++} montmorillonite
ADSORBED, me/100 g
0
25
50
75
100
EQUIL. CONC. me % x 50
0
25
50
75
100
125
150
Na$^+$
K$^+$
NH$_4^+$
Cs$^+$

Figure 9

In Figures 10 and 11 the quantity $\frac{C_{A^+} / C_{Na^+}}{N_{A-Z}}$ is plotted against C_{A^+} / C_{Na^+} for methylammonium and ethylammonium homologues, respectively. Similar "Langmuir" plots are also obtained for the other alkylammonium compounds used. The constants k, b_2/b_1 of equation (37) are obtained from the slope and the intercept of the line. The energy of adsorption of A^+ ions (E_{A^+}) and Na^+ ions (E_{Na^+}) is given by the relationship

$$b_1 / b_2 = - \left[(E_{A^+} - E_{Na^+})/RT \right] \qquad \ldots\ldots(38)$$

In actual fact, the quantity ($E_{A^+} - E_{Na^+}$) is the difference in the free energy of adsorption which is a function of the electrostatic attraction of the cations by the clay surface and the size of the respective cations. The constant k may be identified with the exchange capacity of the clay material which is a constant for any given clay and independent of the nature of the exchangeable cation. Figures 10 and 11 show that for the eight organic cations, the lines are parallel and of equal slope which corresponds to a value of k = 84 me/100 g of clay, in excellent agreement with the experimentally determined value of 86 me /100 g of clay (see Appendix I).

Values of $-(E_{A^+} - E_{Na^+})$ for the alkylammonium cations used, except tetrapropylammonium and tetrabutylammonium ions) are presented in Table 3.

Figure 10.

Langmuir plots for the adsorption of methyl-substituted ammonium cations on Na^+ montmorillonite.

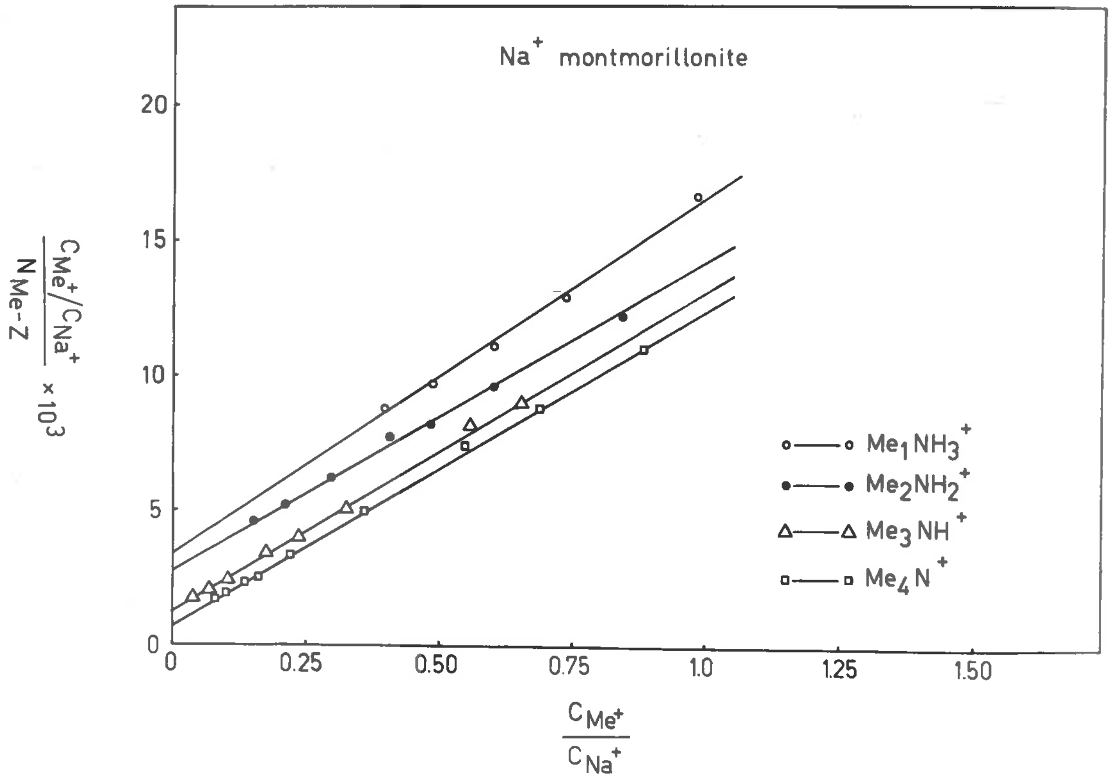
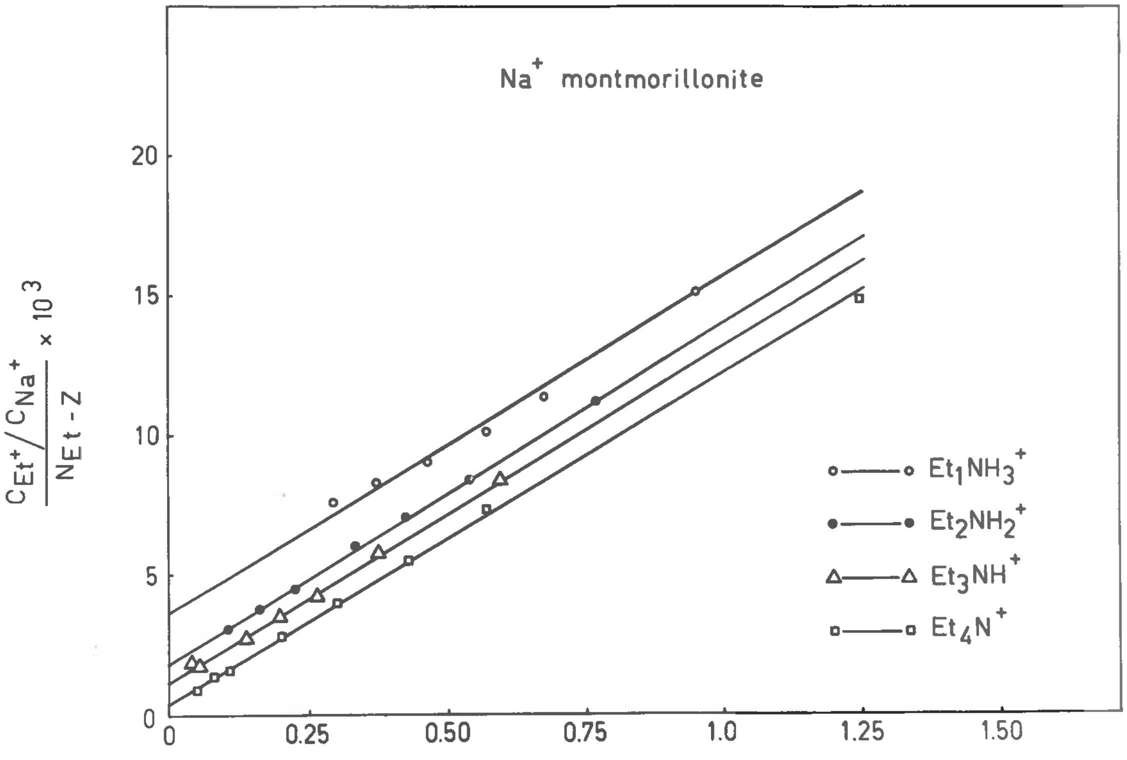

Na$^+$ montmorillonite
$\frac{C_{Me^+}/C_{Na^+}}{N_{Me\text{-}Z}} \times 10^3$
0
5
10
15
20
0
0.25
0.50
0.75
1.0
1.25
1.50
$\frac{C_{Me^+}}{C_{Na^+}}$
$Me_1NH_3^+$
$Me_2NH_2^+$
Me_3NH^+
Me_4N^+

Figure 10

Figure 11.

Langmuir plots for the adsorption of ethyl-substituted ammonium cations on Na^+ montmorillonite.



Na$^+$ montmorillonite
$\frac{C_{Et^+}/C_{Na^+}}{N_{Et-Z}} \times 10^3$
0
5
10
15
20
0
0.25
0.50
0.75
1.0
1.25
1.50
$\frac{C_{Et^+}}{C_{Na^+}}$
$Et_1NH_3^+$
$Et_2NH_2^+$
Et_3NH^+
Et_4N^+

Figure 11

TABLE 3

Difference in free energy of adsorption between alkyl-substituted ammonium cations and sodium ions for montmorillonite.

Cation	$-(E_{A^+} - E_{Na^+})$ (cals/mole)
$Me_1NH_3^+$	667
$Et_1NH_3^+$	650
$Pr_1NH_3^+$	731
$Bu_1NH_3^+$	953
$Me_2NH_2^+$	834
$Et_2NH_2^+$	1132
$Bu_2NH_2^+$	1700
Me_3NH^+	1323
Et_3NH^+	1270
Me_4N^+	1514
Et_4N^+	1931
Pr_4N^+	2265
Bu_4N^+	2437

Positive values for $-(E_{A^+} - E_{Na^+})$ indicate that under the conditions of the experiment, the alkylammonium ion is a better competitor for the clay surface than is the sodium ion.

In the derivation of equations (33) and (34) three assumptions are involved:

(1) the exchange sites on the clay surface are uniform, that is, one site is not preferred to another.

(2) there is no interaction between adsorbed molecules, that is, the sites are sufficiently far apart in comparison to the dimension of the adsorbate molecule.

(3) there is no adsorption of the anion.

For montmorillonite, requirement (1) is likely to be fulfilled since the charge deficiency of the clay material mainly arises from isomorphous replacement within the lattice and the number of positive edge charges, if they exist, can probably be neglected (Edwards and Quirk, 1962). The second and third requirements may become important with large cations such as Pr_4N^+ and Bu_4N^+. In fact, for these two ions, the "Langmuir" plots show deviations from the straight line at high surface coverage, indicating that interaction between adsorbed cations occurs. Inspection of the data shows that only 80 per cent of the sodium ions initially present is replaced at the plateau region ("cover-up" effect). The amount of Pr_4N^+ and Bu_4N^+ ions adsorbed in excess of the amount of sodium ions replaced is accompanied by adsorption of the corresponding anion. Interaction between adsorbed molecules is also apparent since calculation shows that the areas (p. 76) of these ions are slightly greater than the area per exchange site on the interlamellar surface (about 70 $Å^2$ for montmorillonite).

Alternatively, the adsorption process can be treated as a reversible heterogeneous equilibrium represented by equation (22). This treatment is identical with the classical mass-action treatment and has satisfactorily been applied to describe the adsorption of organic compounds by montmorillonite (Slabaugh, 1954; Cowan and White, 1958; Greenland, Laby and Quirk, 1962). The data showed that the exchange reaction between alkylammonium and sodium ions on the clay proceeded in a stoichiometric manner, except for Pr_4N^+ and Bu_4N^+ ions. As has been mentioned earlier, with these two latter ions, only 80 per cent of the sodium ions originally present was replaced, probably due to the "cover-up" effect (Hendricks, 1941). The assumptions made in the derivation of the equilibrium (or mass-action) "constant", K_m, and the free energy change of the ion-exchange process, $-\Delta G^m$, have been discussed in detail in Chapter I. 3. 3.

According to equation (23), a plot of the ratio of the ions in solution, C_{Na^+}/C_{A^+}, against that in the clay phase, N_{Na-Z}/N_{A-Z}, will yield a straight line, passing through the origin the slope of which is equal to $1/K_m$. The mass-action plots for the exchange equilibrium between the methyl- and ethyl- substituted ammonium derivatives and sodium montmorillonite are shown in Figures 12 and 13. The points corresponding to the plateau adsorptions are closest to the origins of the graphs. The initial slope portions of the isotherms are consequently emphasized. Similar plots are obtained for the other compounds used in the present work. When the data of tetrapropyl- and tetrabutylammonium ions are plotted on this basis, a finite intercept is obtained, which is equal to the amount of sodium ions

Figure 12.

Mass-action plots for the adsorption of methyl-substituted ammonium cations on Na^+ montmorillonite.

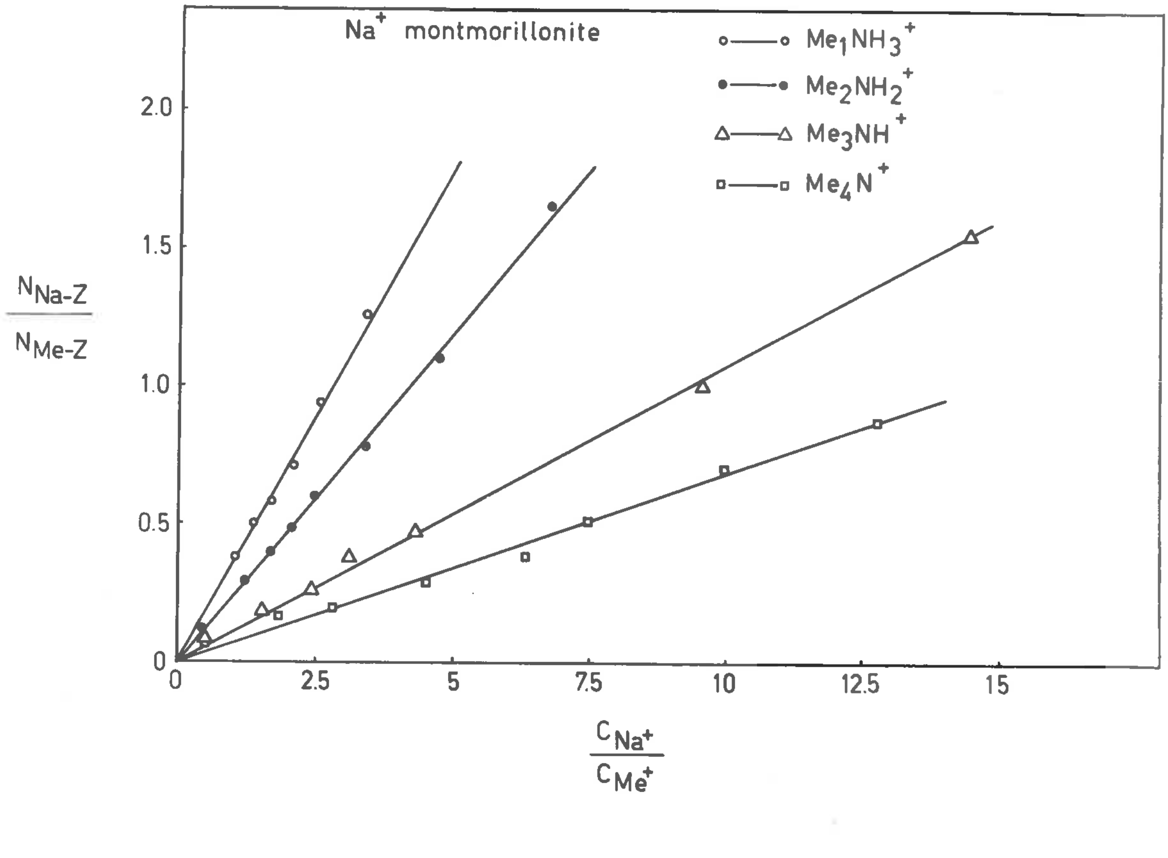

Na$^+$ montmorillonite
Me$_1$NH$_3$$^+$
Me$_2$NH$_2$$^+$
Me$_3$NH$^+$
Me$_4$N$^+$
$\frac{N_{Na-Z}}{N_{Me-Z}}$
$\frac{C_{Na^+}}{C_{Me^+}}$
0
0.5
1.0
1.5
2.0
0
2.5
5
7.5
10
12.5
15

Figure 12

Figure 13.

Mass-action plots for the adsorption of ethyl-substituted ammonium cations on Na^+ montmorillonite.

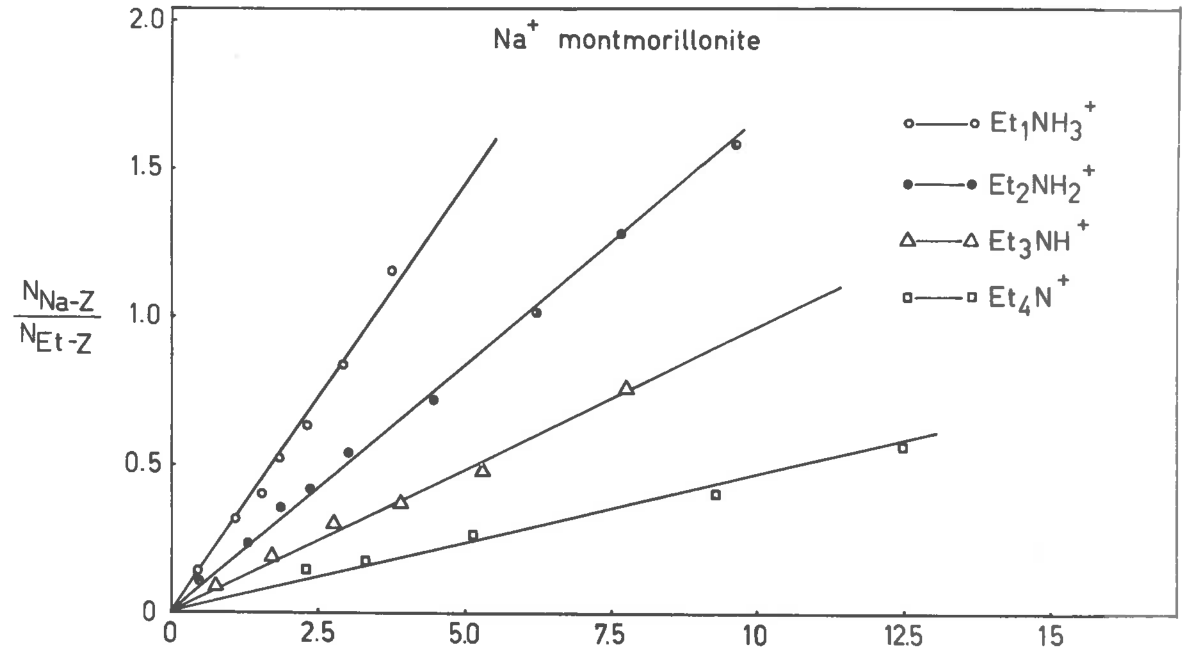

Na$^+$ montmorillonite
$\frac{N_{Na-Z}}{N_{Et-Z}}$
2.0
1.5
1.0
0.5
0
0
2.5
5.0
7.5
10
12.5
15
$\frac{C_{Na^+}}{C_{Et^+}}$
○—○ $Et_1NH_3^+$
●—● $Et_2NH_2^+$
△—△ Et_3NH^+
□—□ Et_4N^+

Figure 13

not replaced by the organic ions ("cover-up" effect). When the mass-action treatment is plotted on the basis that only about 80 per cent of the sodium ions initially present on the clay surface was available to take part in the exchange reaction, the lines for Pr_4N^+ and Bu_4N^+ do pass through the origin.

The free energy change, $-\Delta G^m$, of the exchange reaction is calculated from the relationship:

$$-\Delta G^m = RT \ln K_m \qquad \text{......(39)}$$

Values of K_m and $-\Delta G^m$ are summarized in Table 4.

Table 4.

Mass-action "constants" and free energy change for the exchange equilibrium between alkylammonium compounds and sodium montmorillonite.

Cation	Mass-action "constant" K_m	Free energy change $-\Delta G^m$ (cals/mole)
$Me_1NH_3^+$	2.76	599
$Et_1NH_3^+$	3.03	654
$Pr_1NH_3^+$	3.23	692
$Bu_1NH_3^+$	5.08	960
$Me_2NH_2^+$	4.23	842
$Et_2NH_2^+$	5.83	1041
$Bu_2NH_2^+$	12.67	1500
Me_3NH^+	9.09	1315
Et_3NH^+	9.09	1315
Me_4N^+	14.61	1583
Et_4N^+	21.67	1815
Pr_4N^+	42.55	2213
Bu_4N^+	72.40	2527

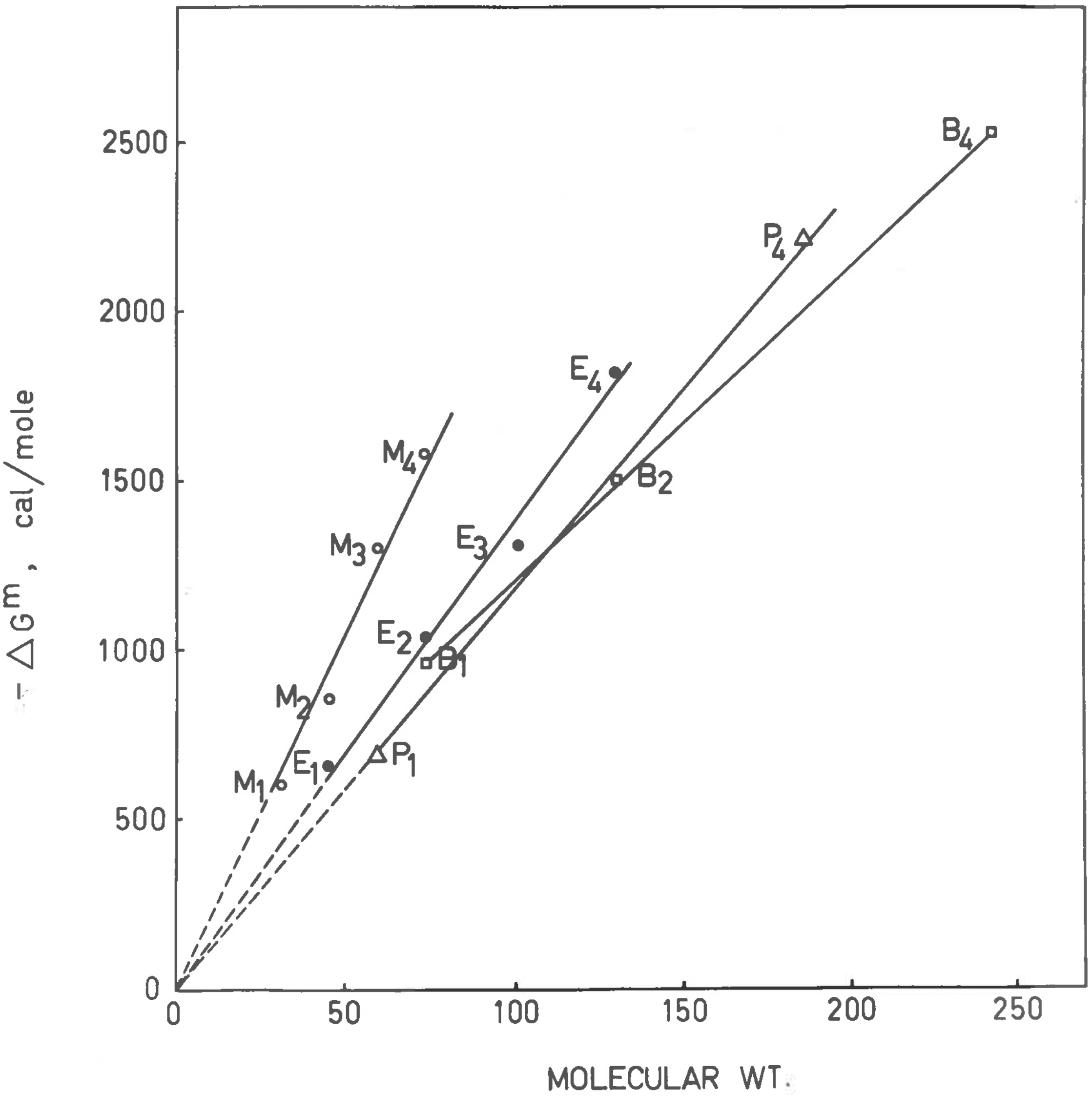
The values of K_m and therefore $- \Delta G^m$ for monoalkylammonium ions obtained in the present instance, are appreciably different from those reported by Cowan and White (1958) and by Slabaugh (1954). However, it must be remembered that K_m is not a true constant but depends on the material used and the experimental conditions.

When $- \Delta G^m$ for each alkylammonium cation is plotted against the corresponding molecular weight of the cation, a straight line is obtained within each homologous series (Figure 14). This means that within each series, the addition of an alkyl group results in a more or less constant increment in $- \Delta G^m$. However, the magnitude of this increment varies between series. The addition of an alkyl group to the central nitrogen atom has a greater effect on the adsorption affinity than addition of the same group to a side chain carbon atom.

These observations can be explained in terms of the size and shape of the organic cation. Within each homologous series, the greater the size of the ion the stronger the bonding stength and therefore the greater $- \Delta G^m$. Variations in $- \Delta G^m$ between homologous series is attributed to steric effects and the basicity of the organic compound. Diamond and Kinter (1961) have reported basal spacing measurements of complexes between montmorillonite and a number of alkylammonium compounds. Their result showed that methyl-substituted ammonium derivatives, because of their compact and spherical shape, could be effectively keyed into the hexagonal depressions of the montmorillonite surface resulting in an apparent contraction of 0.8 - 1.1 Å in the van der Waals thickness of the molecules. For longer alkyl chain derivatives, this contraction was less indicating less intimate contact between the adsorbed molecule and clay surface.

Figure 14.

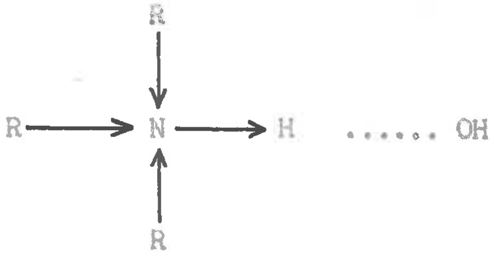
Variation in the free energy change of adsorption with molecular weight for the adsorption of alkyl-substituted ammonium cations on Na^+ montmorillonite.



- ΔG^m , cal/mole
MOLECULAR WT.
0
500
1000
1500
2000
2500
0
50
100
150
200
250
M1
M2
M3
M4
E1
E2
E3
E4
P1
P4
B1
B2
B4

Figure 14

Since the van der Waals forces between two atoms are proportional to r^{-7}, where r is distance between the respective atoms, these forces rapidly fall off as r increases. The contribution of the van der Waals forces to the adsorption energy is greatest for those compounds which can fit best into the clay surface, that is, for the compact methyl-substituted ammonium derivatives. The adsorption affinity is also a function of the basicity of the organic compound. The basic strength of amine compounds increases as the number of alkyl groups increases. This is attributed to the inductive (+ I) effect of the alkyl group. The more alkyl groups attached to the N atom, the greater is the displacement in the N ⟶ H bond. For instance in a compound such as



this displacement gives the hydrogen atom a negative charge which tends to inhibit hydrogen bonding. The greater the negative charge on the hydrogen atom, the less the tendency for hydrogen bonding and thus the smaller the amount of the unionized form. It is to be noted that the inductive effect is a permanent property which rapidly falls off with distance from the nitrogen atom. Basicity can best be expressed in terms of pK_a values of the compound by regarding a substituted ammonium ion as a conjugate acid AH^+, if A is an amine. For the same number of alkyl groups per molecule, the inductive effect results in dimethylammonium ($pK_a = 10.99$) being a stronger base than ethylammonium ($pK_a = 10.63$).

It can therefore be concluded that the interaction between organic cations and montmorillonite can be described either in terms of the simultaneous adsorption of two ionic species for the same sites on the clay surface or in terms of an ion-exchange equilibrium between ions in solution and those at the clay surface.

Adsorption affinities of the organic cation for the clay surface calculated by either treatment are in very good agreement. The relative magnitudes of the adsorption affinity can be related to the size and shape of the molecule and the effect of substituent groups on the basicity of the organic compounds.

(ii) Ca^{++} montmorillonite

a. The shape of the adsorption isotherm

Figures 6 to 9 show the isotherms at 25°C for the adsorption of sodium, ammonium, potassium, cesium and alkyl-substituted ammonium cations by Ca^{++} montmorillonite. All the isotherms conform to the "Langmuir" or L-type (Giles, et al., 1960) and the same general conclusions drawn for Na^{+} montmorillonite are therefore applicable to this instance.

b. Quantitative analysis of the adsorption process

Since the "Langmuir" treatment is essentially identical with the mass-action treatment, only the latter will be considered in this instance.

The expression for the heterogeneous exchange equilibrium involving monovalent ions in solution and calcium ions in the clay phase can be written as

$$2\,A^{+} + \text{Ca-clay} \rightleftharpoons 2\,\text{A-clay} + Ca^{++} \qquad \ldots\ldots(40)$$

The equilibrium or mass action "constant", K_m, for this system is given by

$$K_m = \frac{N^2_{A-Z}}{N_{Ca-Z}} \cdot \frac{C_{Ca^{++}}}{C^2_{A^+}} \qquad \ldots\ldots(41)$$

and when $C_{Ca^{++}}/C^2_{A^+}$ is plotted against N_{Ca-Z}/N^2_{A-Z} a straight line is obtained whose slope equals $1/K_m$. The mass action plots for monovalent inorganic cations and the methyl-substituted ammonium ions are shown in Figure 15 and Figure 16, respectively. When the experimental data for $Et_1NH_3^+$, $Pr_1NH_3^+$, $Bu_1NH_3^+$, and $Et_2NH_2^+$ were plotted according to equation (41) two straight lines of different slopes were obtained (Figure 17). The break between the two portions of the plots corresponds to an amount adsorbed of about 40 me/100 g or about half of the exchange capacity of the clay. Mass-action plots for Et_3NH^+, $Bu_2NH_2^+$, Et_4N^+, Bu_4N^+ yielded a curve whose slope became increasingly larger as the amount of organic cation adsorbed increased indicating that the affinity of the organic ion for the clay surface became smaller as the amount present increased.

These observations can be explained in terms of preferential adsorption on external crystal surfaces and to steric effects due to variations in basal spacing with the amount of organic cation adsorbed. With the smaller and compact methyl-substituted ammonium ions exchange on external and interlamellar surfaces occurred with more or less equal ease as indicated by a "uniform" K_m value over the entire range of concentration. With the second class of compounds ($Et_1NH_3^+$, $Pr_1NH_3^+$, $Bu_1NH_3^+$, $Et_2NH_2^+$) which gave two lines of different slope, exchange for calcium ions up to an amount adsorbed of 40 me/100g was energetically not favourable and K_m in this range was more or less independent of the size of the organic cation. When more than half of the calcium ions initially present had been replaced by the organic ions, K_m increased

Figure 15.

Mass-action plots for the adsorption of sodium, potassium, ammonium, and cesium ions on Ca^{++} montmorillonite.

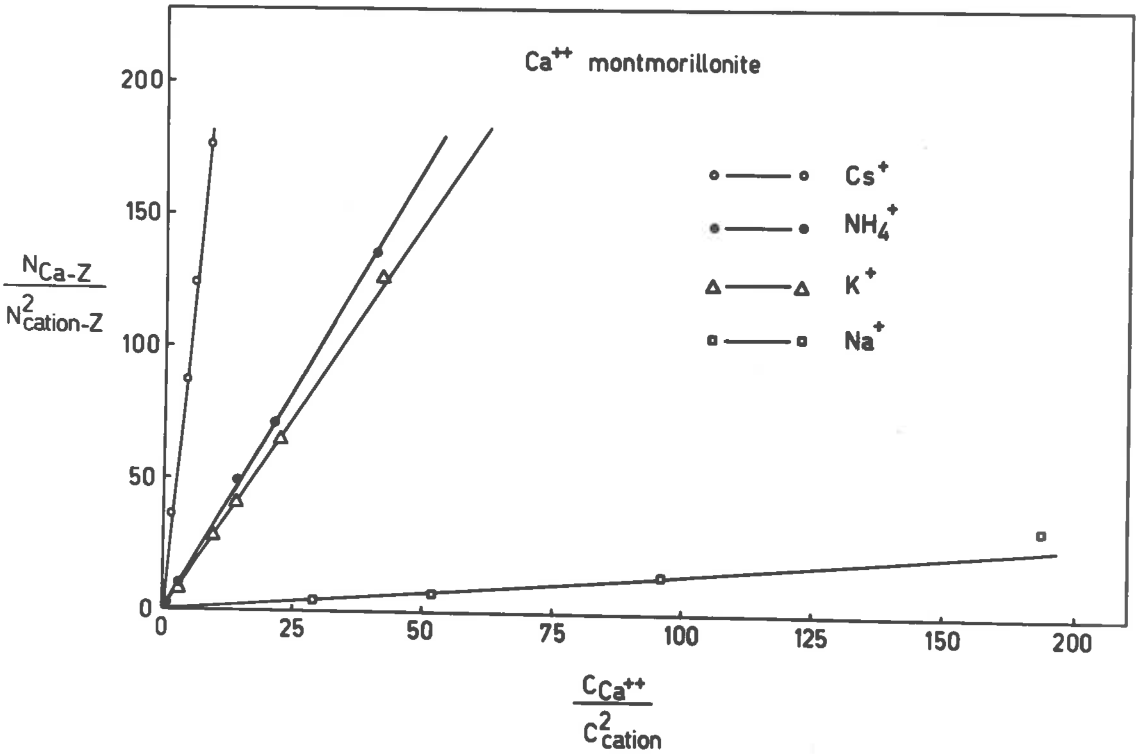
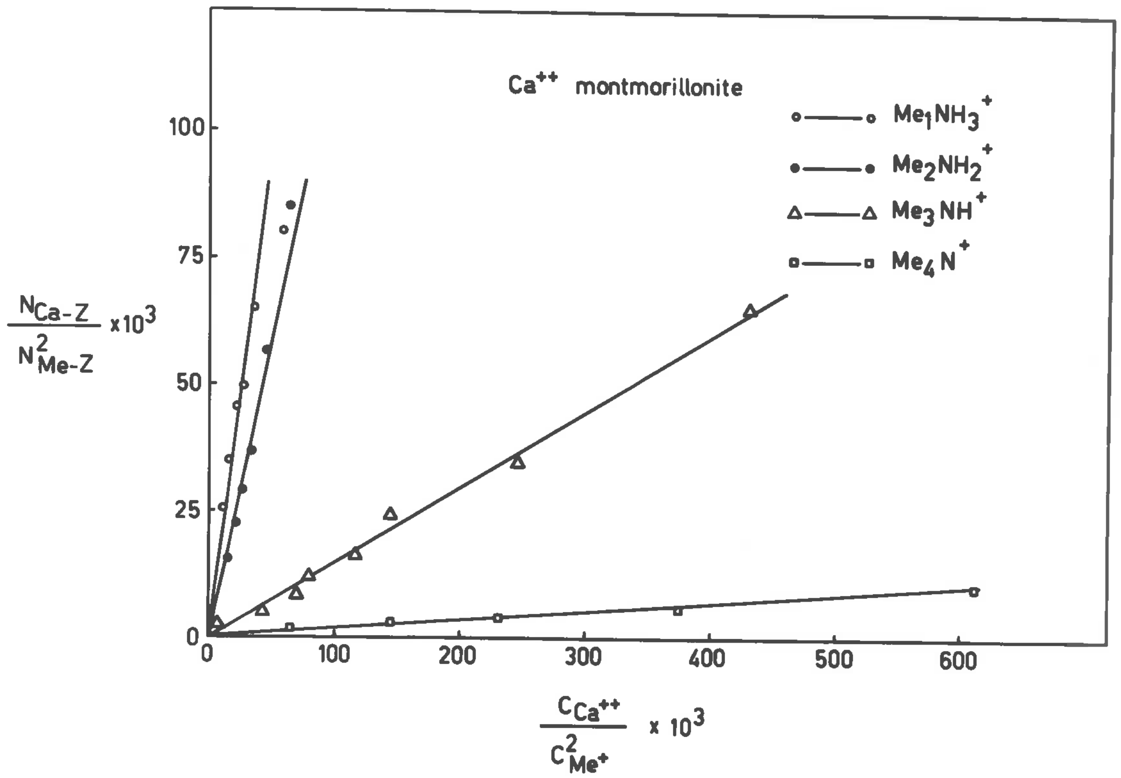

Ca++ montmorillonite
$\frac{N_{Ca\text{-}Z}}{N^2_{cation\text{-}Z}}$
0
50
100
150
200
0
25
50
75
100
125
150
200
$\frac{C_{Ca^{++}}}{C^2_{cation}}$
Cs^+
NH_4^+
K^+
Na^+

Figure 15

Figure 16.

Mass-action plots for the adsorption of methyl-substituted ammonium cations on Ca^{++} montmorillonite.



Ca^{++} montmorillonite
Me$_1$NH$_3^+$
Me$_2$NH$_2^+$
Me$_3$NH$^+$
Me$_4$N$^+$
$\frac{N_{Ca-Z}}{N^2_{Me-Z}} \times 10^3$
0
25
50
75
100
0
100
200
300
400
500
600
$\frac{C_{Ca^{++}}}{C^2_{Me^+}} \times 10^3$

Figure 16

Figure 17.

Mass-action plots for the adsorption of monoethyl-, mono-n-propyl-, mono-n-butyl-, and diethylammonium cations on Ca^{++} montmorillonite.

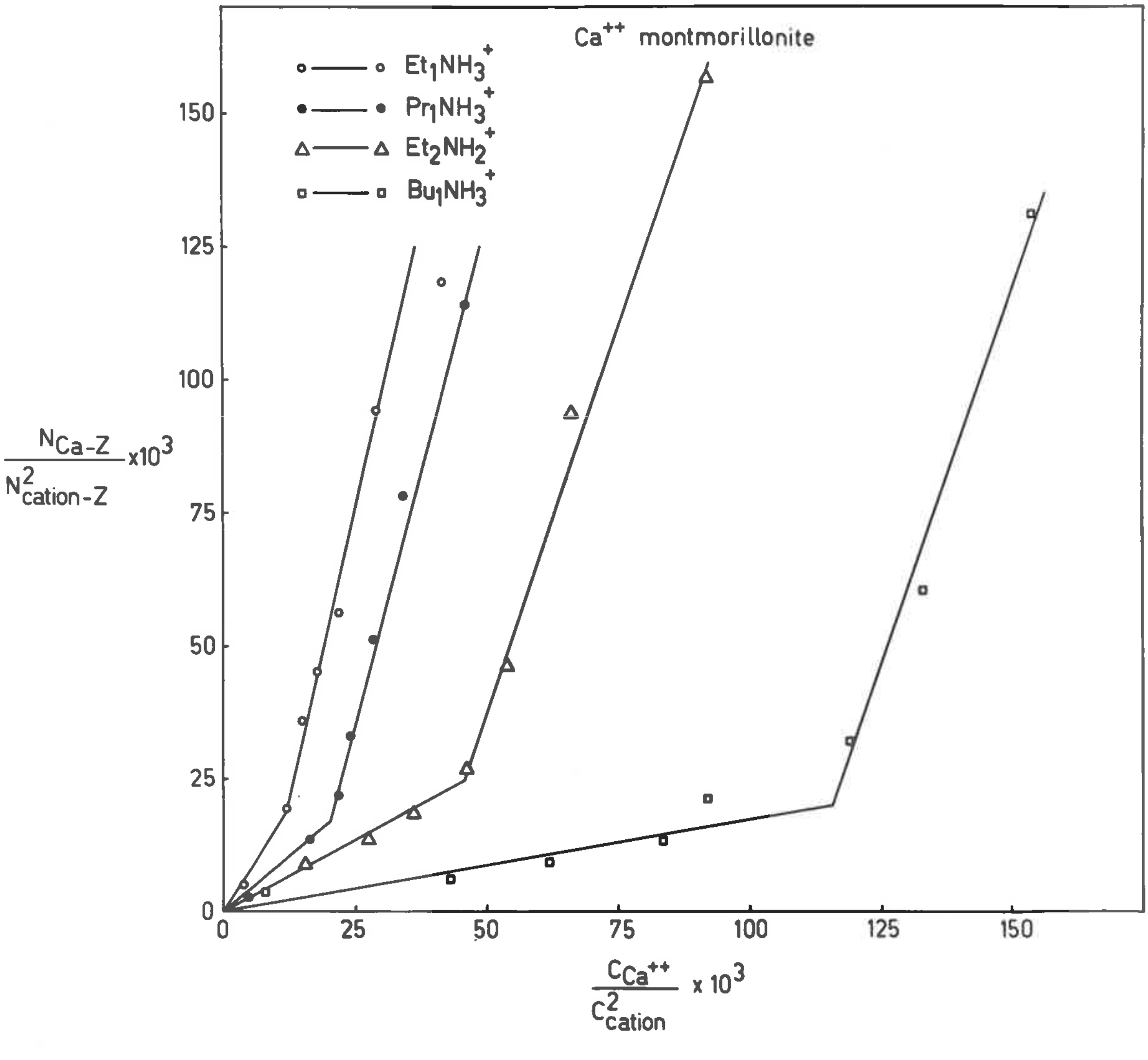

Ca^{++} montmorillonite
Et$_1$NH$_3^+$
Pr$_1$NH$_3^+$
Et$_2$NH$_2^+$
Bu$_1$NH$_3^+$
150
125
100
75
50
25
0
$\frac{N_{Ca-Z}}{N^2_{cation-Z}} \times 10^3$
0
25
50
75
100
125
150
$\frac{C_{Ca^{++}}}{C^2_{cation}} \times 10^3$

Figure 17

and became dependent on the size of the cation. X-ray analysis of the moist complexes showed that the 19 Å basal reflection of the untreated Ca^{++} clay became less sharp as increasing amounts of calcium ions were replaced by alkylammonium cations and this reflection disappeared when about half of the original calcium ions had been replaced. When more than 2/3 of the calcium ions had been exchanged the basal spacing collapsed to 13 Å. The positive value of ΔG^{m} below half saturation by alkylammonium ions was apparently associated with interlamellar expansion and a transition from limited to extensive crystalline swelling. The collapse of the basal spacing when more than 2/3 of the exchangeable calcium ions had been replaced provided the energy for further exchange to occur and the affinity between cation and clay surface increased and became dependent on the size of the organic cation in a similar manner as shown for Na^{+} montmorillonite. With the third class of organic cations (Et_3NH^{+}, $Bu_2NH_2^{+}$, Et_4N^{+}, Bu_4N^{+}) interlamellar separation became increasingly smaller as the amount of organic cations adsorbed increased. It is suggested that the collapse of the interlamellar space on adsorption led to restricted surface migration of the intercalated alkylammonium ions. As the amount of organic cations present increased more energy was required to cause adsorption of an additional amount of alkylammonium ions with a consequent decrease in K_m.

Where the mass action treatment was applicable the free energy change for the exchange reaction could be evaluated from equation (39). Values of K_m and $-\Delta G^{m}$ for the exchange reaction between some inorganic and alkylammonium cations and Ca^{++} montmorillonite are listed in Table 5. Where two straight lines were obtained, two different values of K_m

TABLE 5

Mass-action "constants" and free energy change for the exchange equilibrium between some inorganic and alkylammonium cations and calcium montmorillonite.

Cation	Mass-action "constant"		Free energy change	
	K_m	K_m'	$-\Delta G^m$	$-\Delta G^{m'}$
			(cals/mole)	
Na^+	0.044		-1843	
K^+	0.287		- 735	
NH_4^+	0.344		- 642	
Cs^+	7.50		+1189	
$Me_1NH_3^+$	0.526		- 379	
$Et_1NH_3^+$	0.625	0.218	- 277	- 898
$Pr_1NH_3^+$	1.20	0.235	+ 107	- 855
$Bu_1NH_3^+$	6.76	0.345	+1129	- 626
$Me_2NH_2^+$	0.88		- 21	
$Et_2NH_2^+$	1.80	0.341	+ 347	- 640
Me_3NH^+	8.0		+1227	
Me_4N^+	60.0		+2419	

corresponding to the two slopes were possible. The mass-action "constant" obtained from the second slope of the plot of Figure 17, that is, below an amount adsorbed of 40 me/100 g of clay is denoted by K_m' and the free energy change calculated from K_m' is denoted by $-\Delta G^{m'}$.

CHAPTER III.

X-RAY DIFFRACTION STUDIES

III. 1. Crystalline Swelling of Complexes between Montmorillonite and Alkylammonium Compounds

III. 1. 1. Introduction

X-ray diffraction techniques have been used to obtain direct information on the crystalline swelling of montmorillonite saturated with inorganic and organic cations (Hendricks, Nelson, and Alexander, 1940; Mooney, Keenan, and Wood, 1952b; Norrish, 1954; Diamond and Kinter, 1961; Weiss, 1963). Recently, Barrer and Brummer (1963) have obtained evidence from X-ray studies on complexes between Na^+ montmorillonite and mono- and tetramethylammonium cations that the exchange of sodium ions for the organic cations in the interlamellar regions took place in discrete layers within a crystal resulting in regions which were either predominantly sodium or alkylammonium saturated. Sodium-rich and alkylammonium-rich regions were randomly interstratified. If an interstratification of this nature had occurred the crystalline swelling of the complexes would be expected to be different from that shown by the clay saturated with either sodium and calcium ions or alkylammonium ions alone since the crystalline swelling of Ca^{++} montmorillonite is limited to 19 Å whereas Na^+ montmorillonite shows extensive crystalline swelling and montmorillonite saturated with alkylammonium cations does not expand beyond a basal separation of about 14 Å.

The purpose of the present investigation is to obtain information on the crystalline swelling of montmorillonite containing different amounts of alkylammonium cations on the exchange sites by X-ray diffraction methods, to relate this information to the uptake and retention of water by these complexes and thus have a better understanding of the mechanism by which alkylammonium compounds modify the swelling properties of clays.

In addition to providing information on the crystalline swelling, X-ray diffraction studies also provide useful information on the orientation of the adsorbed cations in the interlamellar region.

III. 1. 2. Experimental

III. 1. 2. 1. Materials

The preparation of the complexes has been described in the preceding chapter.

III. 1. 2. 2. Methods

After decanting the supernatant solution, about 0.1 g of the moist centrifuged material was spread out as a thin film on a porous ceramic tile. The clay film was washed several times by passing distilled water through the tile so as to make the samples comparable to those used for swelling measurements (p. 94). The tile was then covered with a polythene film 0.012 mm thick to minimize water loss by evaporation during exposure to X-rays. The tile was inserted into the sample holder of a Philips X-ray diffractometer P.W. 1050. The specimens were examined with iron-filtered Co radiation, and diffraction diagrams were obtained. On completion of the run, the tile with the clay film was dried in the oven at 70°C overnight and the oven-dry specimens examined.

III. 1. 3. Results

(i) Na^+ montmorillonite

Basal spacings of the moist and oven-dry complexes containing different amounts of alkylammonium cations are listed in Table 6. Data of previous workers are included for comparison.

TABLE 6.

Basal spacings of moist and oven-dry complexes containing given amounts of alkyl-substituted ammonium cations.

Cation	Amount adsorbed, me/100 g	Basal spacing, Å					
		Moist			Oven-dry		
		(1)	(2)	(3)	(1)	(2)	(3)
$Me_1NH_3^+$	76	diffuse	12.6	-	12.5	12.16	12.4
$Et_1NH_3^+$	77	12.75	12.96	-	12.70	12.66	-
$Pr_1NH_3^+$	77	13.20	-	-	12.70	-	-
$Bu_1NH_3^+$	78	13.50	-	-	12.75	-	-
$Me_2NH_2^+$	81	12.85	12.94	-	12.75	12.52	12.2
$Et_2NH_2^+$	82	13.15	13.22	-	13.0	12.81	-
$Bu_2NH_2^+$	87	13.50	-	-	13.20	-	-
Me_3NH^+	84	13.70	13.50	-	13.30	12.84	13.0
Et_3NH^+	81	13.15	13.40	-	13.15	13.26	-
Me_4N^+	86	13.75	14.0	-	13.75	13.85	13.5
Et_4N^+	84	14.0	14.2	-	14.0	14.17	13.9
Pr_4N^+	80	14.70	-	-	14.50	-	-
Bu_4N^+	80	17.0	-	-	15.50	-	-

(1) Present work.

(2) Diamond and Kinter (1961); assumed fully saturated but amount adsorbed not specified. Oven-dried at 110°C.

(3) Data of Barrer and MacLeod (1955), Barrer and Reay (1957) and Barrer and Brummer (1963). All refer to outgassed specimens.

The sharpness of the basal reflections increased as

a. the degree of saturation by alkylammonium cations increased

b. the size of the organic cation increased

With the mono-, di-, and trialkylammonium cations the moist complexes gave diffuse diffraction diagrams below an amount of about 75 me/100 g adsorbed. With tetraalkylammonium cations well-defined basal reflections were obtained when about half of the exchangeable sodium ions had been replaced by the organic cations. After oven-drying the maxima became sharper and at least two higher rational orders were observed for the fully saturated alkylammonium complexes. The increase in sharpness and definition of the oven-dry specimens was probably due to a better orientation of the clay lamellae with respect to each other as water was expelled from the interlamellar region.

Details of the basal spacing data for each alkylammonium cation at different degrees of saturation are presented in Appendix IV.

(ii) Ca^{++} montmorillonite

The moist and oven-dry basal spacings for complexes with alkylammonium and monovalent inorganic cations are presented in Appendix IV. The basal spacings of montmorillonite saturated with alkylammonium cations are about 0.2 Å less than the corresponding complexes prepared from Na^{+} montmorillonite (Table 6). Two classes of complexes can be distinguished on the basis of the variation in the moist basal spacing as a function of the amount of alkylammonium cations adsorbed.

a. Complexes with monoalkylammonium, dimethyl- and trimethylammonium. The 19 Å basal reflection of the moist Ca^{++} montmorillonite gradually decreased in sharpness as the amount of organic cations present increased. When about 40 me/100 g had been adsorbed the 19 Å line was absent and the diffraction diagrams became diffuse similar to that shown by moist Na^{+} montmorillonite. When more than 2/3 of the original Ca^{++} ions present had been replaced by the organic cations a basal spacing characteristic of each cation was observed (12.5 Å - 14 Å). This reflection increased in sharpness up to full saturation by the organic cation.

b. Complexes with dibutyl-, triethyl- and tetraalkyl-ammonium cations. In this instance the basal spacing of the moist complexes decreased as the amount of organic cation adsorbed increased. No transition from sharp to diffuse patterns or vice versa was observed.

III. 1. 4. Discussion

Since important differences were observed between the crystalline swelling of complexes prepared from sodium and those prepared from Ca^{++} montmorillonite the results will be discussed separately.

(i) Na^{+} montmorillonite

It is known that sodium montmorillonite can overcome the potential barrier of limited crystalline swelling and shows extensive crystalline swelling when immersed in water and dilute electrolyte solutions (Norrish, 1954). Under these conditions diffuse double layers are formed resulting in large interlamellar separations [d(001)> 100 Å] which could not be measured by the methods used in this work. The diffraction patterns for the moist untreated Na^+ montmorillonite were therefore diffuse . The appearance of a well-defined basal reflection when a given amount of alkylammonium cations was adsorbed indicates that diffuse double layers had collapsed on the clay surfaces and that extensive crystalline swelling had given way to limited crystalline swelling similar to that shown by Ca^{++} montmorillonite. The transition from extensive to limited crystalline swelling occurred when more than 2/3 of the exchange sites had been occupied by the organic cations (slightly less for the larger cations).

The basal spacings of the oven-dry complexes showed an increase with the amount of alkylammonium cations adsorbed (see Appendix IV). These observations are consistent with similar results obtained by Barrer and Brummer (1963) and can be interpreted in terms of random interstratification of regions predominantly saturated either with alkylammonium or sodium ions. It seems likely that collapse of diffuse double layers occurred in discrete layers within a crystal whilst other layers were still fully expanded. This postulate is supported by the fact that the basal reflection of the moist complexes increased in definition and sharpness as the amount of organic cations on the complex increased.

An inspection of Table 6 reveals that the basal spacing of montmorillonite saturated with alkylammonium cations decreased on oven-drying. This decrease is attributed to the expulsion of water molecules associated with the interlamellar surface or with the organic cation.

The magnitude of the contraction in the basal spacing on oven-drying decreased with the size of the organic ion in agreement with the results of Diamond and Kinter (1961). These workers observed that when the organic cation contained six or more carbon atoms the difference between the basal spacing of moist and oven-dry complexes was not greater than 0.1 Å. This observation is probably due to the increase in the hydrophobic property of the organic cation as the number of alkyl groups per molecule increases and hence the amount of water associated with the cation decreases. Tetrabutylammonium montmorillonite forms an exception to the above rule. The oven-dry spacing of this complex was appreciably less than the moist basal spacing. This large decrease in basal spacing could be attributed to either the expulsion of water or to a re-organization to give a denser packing of the cations in the interlamellar space. However, the tetrabutylammonium ion is not hydrated (Robinson and Stokes, 1955, p. 120). For this reason, the contraction of the basal spacing on oven-drying is perhaps more likely to be due to a re-orientation and re-arrangement of the interlamellar cations so as to present maximum contact with the clay surface.

An inspection of Table 6 shows that no more than a monolayer of organic cations was present in the interlamellar region since the thickness of the montmorillonite lamella is 9.5 Å (p. 72) and the thickness of a methyl group is given as 4 Å (Pauling, 1960, p.260).

(ii) Ca^{++} montmorillonite

The variation in the basal spacing of moist complexes as a function of the amount of alkylammonium cations adsorbed, is the most noteworthy feature of the results. When about half of the exchange sites had been occupied by monoalkyl-, dimethyl- and trimethylammonium ions [class (a)] the limited crystalline swelling gave way to extensive crystalline swelling. The transition from limited to extensive crystalline swelling is indicated by the disappearance of the 19 Å basal reflection, characteristic of moist Ca^{++} montmorillonite, to give a diffuse diffraction diagram as shown by moist Na^{+} montmorillonite. It is proposed that as an interlamellar calcium ion was replaced by two monovalent alkylammonium cations entropy was gained. This gain in entropy is attributed to the disruption of the ordered water structures around the calcium ion by the organic cation. Entropy can also be gained when the two "links" between an interlamellar calcium ion and opposing clay lamellae are broken by exchange with a monovalent alkylammonium ion. The entropy thus gained enables the calcium ion to overcome the potential barrier of limited crystalline swelling with a consequent formation of diffuse double layers between the lamellae.

The gradual decrease of the 19 Å basal line with increasing amounts of alkylammonium cations adsorbed below 45 me/100 g indicates random interstratification of calcium-rich and alkylammonium-rich layers within a single crystal. The formation of diffuse double layers presumably occurred in those layers within a crystal where exchange for alkylammonium cations was preferred. The repulsive potential associated with the formation of diffuse double layers would be expected to separate such layers from the remainder of the crystal resulting in a decrease in mean crystal size.

On the other hand, when more than 2/3 of the calcium ions initially present had been replaced by alkylammonium ions, the reverse process took place, that is, extensive crystalline swelling gave way to limited crystalline swelling with a consequent collapse of diffuse double layers. This collapse was indicated by the appearance of a well-defined basal reflection which increased in sharpness with the amount of alkylammonium ions adsorbed. The collapse of diffuse double layers would be expected to result in an increase in the mean number of lamellae making up a crystal.

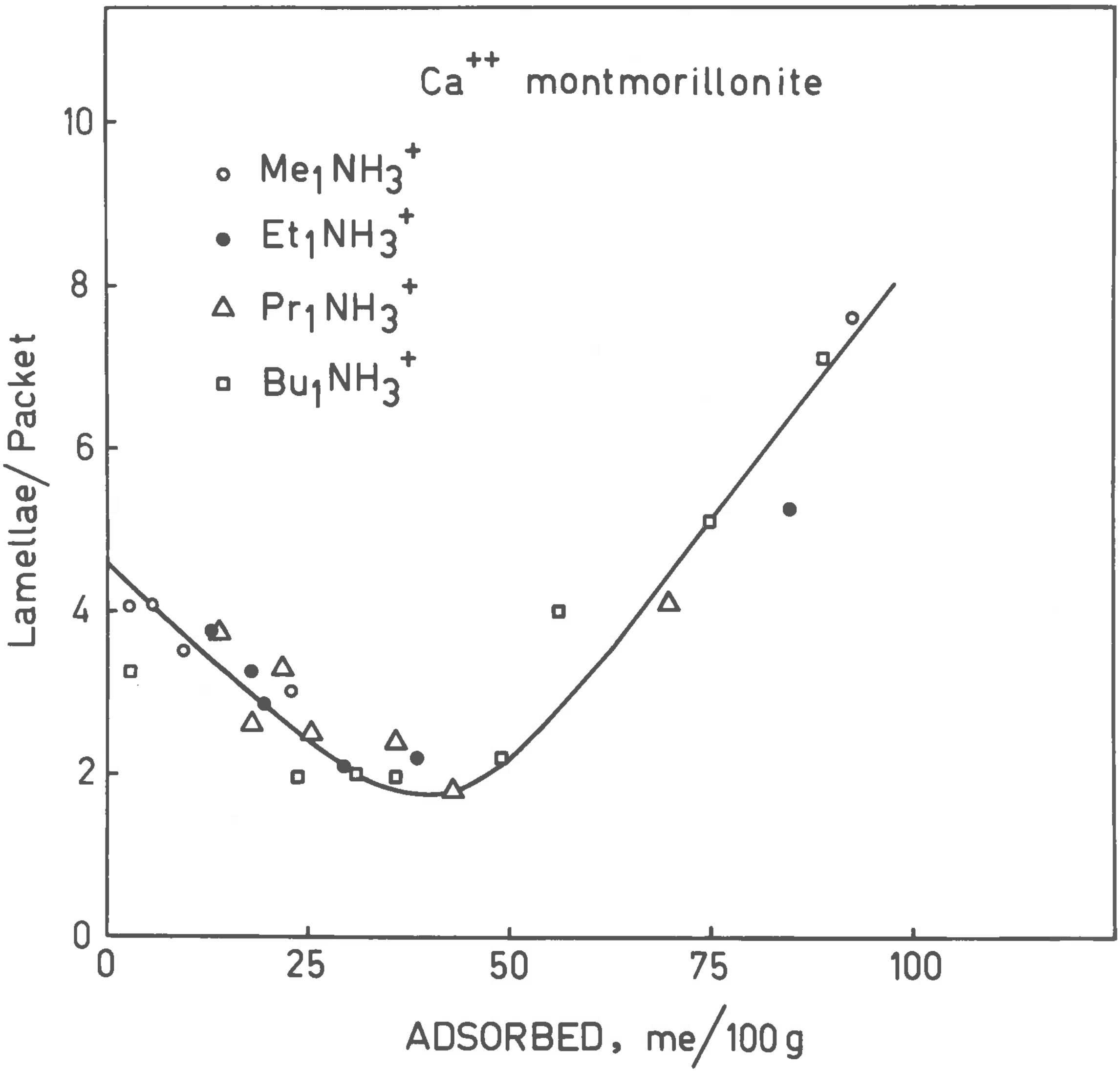
The mean number of lamellae making up a crystal (L) can be estimated from the broadening of the basal reflection line by the method first studied by Scherrer (Blackmore and Miller, 1961). Details of this method and calculation of L for complexes containing different amounts of monoalkylammonium ions are presented in Appendix V. The results of this calculation are shown in Figure 18. The calculation is based on the assumption that line broadening is due only to small crystal size and not to imperfect crystal structure or interstratification effects.

It is interesting to note (Figure 18) that the number of lamellae per crystal decreased from about 5 to about 2 as the number of alkylammonium ions present increased from zero to 45 me/100 g of clay. A further increase beyond this amount adsorbed resulted in an increase of L to about 8. Because of the assumptions involved it is probable that L is an underestimate. The apparent decrease in L as the amount of monoalkylammonium ions increased to 45 me/100 g may well be due to interstratification of layers showing extensive crystalline swelling with those having a basal spacing of 19Å.

With $Bu_2NH_2^+$, Et_3NH^+, and tetraalkylammonium ions [class (b)] swelling was limited for any given amount of organic cation adsorbed. The tendency to form diffuse double layers was probably counteracted

Figure 18.

Variation in mean number of lamellae per crystal (packet) with amount of monoalkylammonium cations adsorbed by Ca^{++} montmorillonite.



Ca^{++} montmorillonite
○ $Me_1NH_3^+$
● $Et_1NH_3^+$
△ $Pr_1NH_3^+$
□ $Bu_1NH_3^+$
Lamellae/ Packet
0
2
4
6
8
10
0
25
50
75
100
ADSORBED, me/100 g

Figure 18

by the greater attraction between clay lamellae due to an increase in adsorption affinity and hydrophobic property of the organic cation as the size of the cation increased. Attraction exceeds repulsion for any given amount of organic cations present as indicated by a gradual collapse of the basal spacing of the moist complexes from 19 Å to about 14 Å.

III. 2. Interlamellar Separation and Orientation of Adsorbed Molecules

It is customary to discuss X-ray diffraction results in terms of the difference between the observed basal spacing [d(001)] of the clay-organic complex and the thickness of the clay lamella, t (see Figure 1b). This difference is referred to as the Δ-value (MacEwan, 1948a; Greene-Kelly, 1955b). Δ- values are compared with the minimum van der Waals thickness of the molecules estimated from "Catalin" molecular models. The dimensions of these models were measured with a vernier reading to 0.1 mm. Since the atomic dimensions of the model are smaller than the generally accepted van der Waals radii as given by Pauling (1960, p. 260) the measured thickness must be corrected to obtain true scale representation. The "Catalin" atomic dimensions and Pauling's van der Waals radii are listed in Table 7.

TABLE 7

van der Waals radii measured from "Catalin" atomic models and according to Pauling (1960, p. 260).

Atom or group	van der Waals radius, Å	
	"Catalin"	Pauling
Hydrogen	0.95	1.2
Methyl and Methylene	1.75	2.0

Δ- values and the corresponding molecular thickness for each alkyl-substituted ammonium compound are listed in Table 8.

It has been shown (Greene-Kelly, 1955b) that on heating in vacuo montmorillonite saturated with inorganic cations of different size gives a minimal d(001) spacing of 9.5 Å. This spacing is independent of the radius of the exchangeable cation, provided that it does not exceed 1.2 Å. In calculating Δ- values, the thickness of the montmorillonite lamella is therefore taken as 9.5 Å instead of the calculated thickness (9.4 Å) derived from considerations of atomic dimensions. Δ- values listed in Table 8 refer to complexes saturated with alkylammonium cations prepared from Na^+ montmorillonite (see Table 6). These values are about 0.2 Å greater than the corresponding values for complexes prepared from Ca^{++} montmorillonite.

TABLE 8

Δ- value, minimum molecular thickness and apparent contraction of alkyl-substituted ammonium cations on adsorption by montmorillonite.

Cation	Δ- value, Å	Minimum molecular thickness, Å		Apparent contraction, Å
		"Catalin"	Corrected	
$Me_1NH_3^+$	3.10	3.23	3.7	0.6
$Et_1NH_3^+$	3.30	3.40	3.9	0.6
$Pr_1NH_3^+$	3.30	3.40	3.95	0.65
$Bu_1NH_3^+$	3.35	3.45	4.0	0.65
$Me_2NH_2^+$	3.35	3.40	3.9	0.55
$Et_2NH_2^+$	3.60	3.52	4.0	0.40
$Bu_2NH_2^+$	3.80	3.67	4.2	0.40
Me_3NH^+	3.90	3.84	4.3	0.40
Et_3NH^+	3.75	4.25	4.7	0.95
Me_4N^+	4.35	4.75	5.3	0.95
Et_4N^+	4.60	4.9	5.5	0.90
Pr_4N^+	5.10	-	-	-
Bu_4N^+	5.70	-	-	-

No precise thickness can be assigned to tetrapropyl- and tetrabutylammonium cations since for these ions many configurations are possible. It is likely that the apparent contraction in the van der Waals thickness for these two cations is of the same order of magnitude as for tetramethyl- and tetraethylammonium ions.

The apparent contraction in the van der Waals thickness of the adsorbed cation ranges from 0.4 to 0.95 Å. By using the same model for the montmorillonite surface as described by Greenland, Laby, and Quirk (1962) it was possible to "key" the cations into the hexagonal depressions of the silicate surface to give contractions equal or greater than those observed. Specific bonding mechanisms such as C-H ... O hydrogen bonding between the methylene groups of the cation and the oxygen atoms of the silicate surface (Bradley, 1945; MacEwan, 1948a) need therefore not be invoked to account for the observed contractions of the cations on adsorption.

It has been assumed in the discussion of basal spacings and apparent contractions in the van der Waals thickness of the adsorbed cations that these ions are oriented so as to present their minimum thickness in the direction perpendicular to the clay lamellae. Recently, Rowland and Weiss (1961) have put forward the suggestion that monomethyl- and dimethyl-ammonium cations may be adsorbed in an orientation such as to present their long axes perpendicular to the clay lamellae with considerable keying of the cations into the hexagonal oxygen holes of the silicate surface. Such an orientation in this instance was possible from a consideration of Δ- values for these two cations measured by using models of the montmorillonite surface and the molecule.

III. 3. Molecular Areas and Surface Coverage

The external crystal area of Redhill montmorillonite was obtained by applying the isothermal equation of Brunauer, Emmett, and Teller (B.E.T.) to liquid nitrogen adsorption data, assigning a value of 16.2 $Å^2$ to the area occupied by a single nitrogen molecule. The area thus obtained was 120 m^2/g. The total surface area of the clay (external and interlamellar) was estimated from adsorption of cetylpyridinium bromide (Theng,1961; Greenland and Quirk, 1962). This method yields a surface area of 800 m^2/g. If the exchange sites are uniformly distributed over the entire surface area of the clay, 15 per cent of these sites are present on external crystal surfaces and 85 per cent in the interlamellar region. Since in the latter instance an alkylammonium cation is shared between two opposing lamellae the area covered by the cation must be multiplied by two.

The area per cation was estimated from "Catalin" molecular models corrected for Pauling's van der Waals radii and assuming that the adsorbed cation was oriented so as to present its minimum thickness in the direction perpendicular to the clay lamellae. Following Greenland, Laby, and Quirk (1962) two different estimates of limiting molecular areas are possible,

a. the area described by the projection of the cation on a flat planar surface, denoted by A_p

b. the area contained within the smallest rectangle which can be described around (a), denoted by A_r

The surface coverage corresponding to A_p and A_r expressed as a fraction of the total surface area of the clay, is denoted by θ_p and θ_r, respectively.

Values of A_p and A_r and those of θ_p and θ_r for each alkyl-substituted ammonium cation at the given amount adsorbed are listed in Table 9.

TABLE 9

Molecular areas of alkylammonium cations and surface coverage when 86 me of cations are adsorbed per 100 g clay.

Cation	Molecular area, Å^2.		Surface coverage	
	A_p	A_r	θ_p	θ_r
$Me_1NH_3^+$	11.8	13.2	0.14	0.16
$Et_1NH_3^+$	17.5	24.0	0.21	0.29
$Pr_1NH_3^+$	23.3	29.0	0.28	0.35
$Bu_1NH_3^+$	25.4	32.7	0.30	0.39
$Me_2NH_2^+$	16.3	24.5	0.20	0.29
$Et_2NH_2^+$	24.5	33.5	0.29	0.40
$Bu_2NH_2^+$	41.7	59.0	0.50	0.70
Me_3NH^+	21.8	30.0	0.26	0.36
Et_3NH^+	35.7	54.7	0.43	0.65
Me_4N^+	23.0	31.0	0.27	0.37
Et_4N^+	39.0	45.0	0.47	0.54
Pr_4N^+	58.0	77.0	0.69	0.92
Bu_4N^+	78.0	110	0.93	>1.0

The packing of the adsorbed molecules on the clay surface is not known. However, the infra-red spectra of complexes with tetraalkylammonium ions (see III. 4) showed that the conformation of the adsorbed cations is not significantly different from that of the ion in aqueous solution. The infra-red spectra also confirm that rotational isomers exist in the adsorbed phase and in the chloride and bromide salts. For these reasons it is considered that it is probably best to assume that the adsorbed molecules occupy an area equivalent to the smallest containing rectangle (A_r). For a large cation such as tetrabutyl ammonium it is probable that some adjustment occurred at high surface coverage. Calculation of surface coverage by tetrabutylammonium using the value of A_r = 110 Å^2 showed that when 65 me/100 g was adsorbed the total surface area of the clay was covered. Adsorption in excess of this amount probably resulted in a tighter packing and adjustment of the adsorbed molecule. This re-orientation is indicated by the increase in the basal spacing of the oven-dry specimen from 14.7 Å to 15.5 Å, when 65 and 84 me/100 g were present, respectively. Under this condition A_p is probably a better estimate of the area occupied by the cation. For triethylammonium ion A_r is probably a large overestimate because of the triangular shape of this cation and hence A_p is chosen in this instance.

Values of surface coverage for different amounts of alkylammonium cations adsorbed are presented in Appendix VI.

III. 4. Infra-red Spectroscopy and the Structure of Adsorbed Cations

III. 4. 1. Introduction

In the foregoing discussion of X-ray diffraction data it has been assumed that there was little or no increase in the distortion of bond angles of the molecule (cation) in the adsorbed phase. Because of interaction between adsorbed molecules and adsorption forces between molecule and clay surface deformation of bond angles and alteration in structural configuration of adsorbed molecules are to be expected. Both molecular interaction and adsorption forces increase with the size of the molecule and at high surface coverage.

Infra-red spectroscopy provides a useful method for obtaining information on the conformation of the adsorbed molecule. The infra-red spectra of complexes with tetraalkyl-ammonium cations have therefore been studied. These spectra were compared to those obtained for the compounds in aqueous solution and in the solid state. The infra-red studies reported here were carried out by Dr. R.H. Laby.

III. 4. 2. Experimental

III. 4. 2. 1. Materials

The preparation of the complexes has been described in chapter II. 2. 2. The details of the complexes and salts studied are given in Table 10.

TABLE 10.

Details of ammonium and tetraalkylammonium salts and their complexes with montmorillonite studied by infra-red spectroscopy.

Cation	Anion in the salt	Complex with montmorillonite Amount adsorbed (me/100 g)	 Amount of Na^+ retained (me/100 g)
NH_4^+	Cl^-	83	3
Me_4N^+	Br^-	85.6	0.4
Et_4N^+	Br^-	87	0
Pr_4N^+	I^-	71.5	14.5
Bu_4N^+	I^-	88	0

III. 4. 2. 2. Methods

The spectra were studied between 2 μ and 15 μ (5000 to 667 cm^{-1}) using a Perkin Elmer model 221 spectrometer, a double beam instrument equipped with a single pass sodium chloride prism monochromator.

To obtain the spectra of the solid salts and complexes, an approximately 2 mg sample was ground with 150 mg KCl or KBr and pressed at 55 tons per square inch in a 15 mm diameter evacuated die. Preliminary studies with the solid samples supported in perfluorohydrocarbon oil demonstrated that reliable spectra were obtained using the potassium chloride discs (Baker, 1957). The spectra of aqueous solutions of ammonium chloride and tetramethyl- and tetraethylammonium bromide were also studied.

III. 4. 3. Results

The results are summarized in Table 11. The assignments given in Table 11 were obtained from consideration of the data of the present work, and related data for oriented films of ammonium and tetraalkylammonium vermiculites (Laby and Theng, 1964).

III. 4. 4. Discussion

(i) The spectrum of ammonium ions and their complexes with montmorillonite

Badger (1940) has pointed out that for hydroxyl compounds, the displacement of the frequencies of the hydrogen bonded band from that of the free hydroxyl ($\Delta\nu$) provides a delicate measure of the force constant of the OH ... O bond and varies inversely with the bond length. This concept has been extended to include N-H ... O hydrogen bonds. The infra-red spectra, structure and hydrogen bonding in ammonium salts have been studied by Waddington (1958). Some of Waddington's data are compared with the data obtained from the present studies in Table 12.

TABLE 11

Frequencies (cm^{-1}) and assignments for salts and complexes studied.

Ammonium

NH_4Cl KCl disc	NH_4Cl aq. solution	NH_4^+ montmorillonite	Assignments
3145 (vs)	-*	3193	ν_3
3029 (vs)	3058	3040	$\nu_2 + \nu_4$
2808 (s)	2882		$2\nu_2$
1751 (m, br)	-	-	$\nu_4 + \nu_6$
1445 (s sh)	1449	1411	ν_4
1418 (vs)			)
1408 (vs)			) ν_4
1046 (v br)			

v = very; s = strong; sh = shoulder; m = medium; br = broad.

-* obscured by absorption of supporting phase; - absent.

Table 11, continued.

Tetramethylammonium

Me_4NBr KCl disc	Me_4NBr aq. solution	Me_4N^+ montmorillonite	Assignments
3390 (br)			overtones, combination bands
3022 (sp)	-*	-*	asymmetric C-H stretch, N-methyl
2933 (br)			Fermi resonance with 2X 1491
2780 (w)			symmetric C-H stretch, N-methyl
1491 (s,sp)	1488 (sp)	1491 (sp)	asymmetric C-H deformation, N-methyl
1405 (m,sp)	1419 (vw)	1420 (w)	symmetric C-H deformation, N-methyl
1399 (w,sp)			
1405 (m,sp)	1419 (vw)	1420 (w)	asymmetric deformation of $N-C_4$ skeleton
1399 (w,sp)			
1295 (vw)			
959 (ms,sp)			
951 (s,sp)			
920 (wsh)			

Table 11, continued.

Tetraethylammonium

Et_4NBr KBr disc	Et_4NBr aq. solution	Et_4N^+ montmorillonite	Assignments
3477 (br)			overtones, combination bands
2993 (sp)	-*	2986 (sp)	asymmetric C-H stretch, C-methyl
2945 (sh)		(vwsh)	asymmetric C-H stretch, methylene, strained conformation
1625 (w)			overtone, combination band
1495 (sp)	1488 (s)	1492 (s,sp)	N methylene sciss., flat (strained)conf.
1475 (vwsh)	1475 (sh)		asymmetric C-H deform., C-methyl
	1459 (m)	1463 (w)	methylene sciss., tetrah. (unstrained) conf.
1446 (s)	1444 (sh)	1446 (w)	asymmetric C-H deform., C-methyl
1407 (m)	1407 (vwsh)	1398 (s)	asymmetric deformation of $N-C_4$ skeleton
1401 (ms)	1397 (s)		
1374 (m)	1368 (w)	1376 (w)	symmetric C-H deform., C-methyl
1338 (w)			N methylene wag, flat (strained) conf.
	1305 (w)		methylene wag, tetrah. (unstrained) conf.
1189 (m)	1184 (wsh)		
1175 (s)	1173 (m)		
1070 (w)			
1047 (m)		1031 (wsh)	
1011 (sh)			
1004 (s)		1002 (s)	
897 (w)			
800 (s)			
786 (ms)			methylene rock

Table 11, continued.

Tetraethylammonium

Et_4NBr KBr disc	Et_4NBr aq. solution	Et_4N^+ montmorillonite	Assignments
3477 (br)			overtones, combination bands
2993 (sp)	-*	2986 (sp)	asymmetric C-H stretch, C-methyl
2945 (sh)		(vwsh)	asymmetric C-H stretch, methylene, strained conformation
1625 (w)			overtone, combination band
1495 (sp)	1488 (s)	1492 (s,sp)	N methylene sciss., flat (strained) conf.
1475 (vwsh)	1475 (sh)		asymmetric C-H deform., C-methyl
	1459 (m)	1463 (w)	methylene sciss., tetrah. (unstrained) conf.
1446 (s)	1444 (sh)	1446 (w)	asymmetric C-H deform., C-methyl
1407 (m)	1407 (vwsh)	1398 (s)	asymmetric deformation of $N-C_4$ skeleton
1401 (ms)	1397 (s)		
1374 (m)	1368 (w)	1376 (w)	symmetric C-H deform., C-methyl
1338 (w)			N methylene wag, flat (strained) conf.
	1305 (w)		methylene wag, tetrah. (unstrained) conf.
1189 (m)	1184 (wsh)		
1175 (s)	1173 (m)		
1070 (w)			
1047 (m)		1031 (wsh)	
1011 (sh)			
1004 (s)		1002 (s)	
897 (w)			
800 (s)			
786 (ms)			methylene rock

Table 11, continued.

Tetrapropylammonium

Pr_4NI KCl disc	Pr_4N^+ montmorillonite	Assignments
3411		overtones, combination bands
2979 (s,sp)	2986 (s,sp)	asymmetric C-H stretch, C-methyl
2955 (wsh)	2955 (sh)	asymmetric C-H stretch, methylene, unstr. conf.
2882 (m,sp)	2889 (sp)	symmetric C-H stretch, C-methyl
	1492 (s,sp)	N methylene sciss., flat (strained) conf.
1475 (s,sp)		asymmetric C-H deform., C-methyl
	1465 (br,sh)	
1460 (m)		methylene sciss., tetrah. (unstrained) conf.
1442 (sh)		asymmetric C-H deform., C-methyl
1397 (w)	1393 (w)	asymmetric deform. of $N-C_4$ skeleton
1361 (vw)		symmetric C-H deform., C-methyl
1331 (vw)		N methylene wag, flat (strained) conf.
1322 (vw)		methylene wag, tetrah. (unstrained) conf.
1272 (w)		
1172 (w)		
1040 (m)		
986 (m)		
971 (m)		
751 (m)		methylene rock

Table 11, continued.

Tetrabutylammonium

Bu_4NI KCl disc	Bu_4N^+ montmorillonite	Assignments
2963 (sp)	2967 (sp)	asymmetric C-H stretch, C-methyl
	2946 (wsh)	asymmetric C-H stretch, methylene, str. conf.
2927 (wsh)		asymmetric C-H stretch, methylene, unstr. conf.
2876 (sp)	2876 (sp)	symmetric C-H stretch, C-methyl
	1486 (m)	N methylene sciss., flat (strained) conf.
1474 (s,sp)		asymmetric C-H deform., C-methyl
1464 (s,sp)	1464 (vbr,sh)	methylene sciss., tetrah. (unstrained) conf.
1456 (ms,sp)		asymmetric C-H deform., C-methyl
1382 (m)	1382 (m)	asymmetric deform. of $N-C_4$ skeleton
1365 (w)		symmetric C-H deform., C-methyl
1323 (w)		methylene wag, tetrah. (unstrained) conf.
1239 (w)		
1179 (vw)		
1168 (m)		
1110 (s)		
1066 (w)		
1057 (wsh)		
1030 (m)		
922 (s)		
896 (s)		
881 (s)		
736 (s)		methylene rock

Legend to Table 11. v = very; s = strong; sh = shoulder; sp = sharp; m = medium; w = weak; br = broad -* obscured by absorption of supporting phase; - absent.

Underlined figures obtained from spectra run at 8 cm = 1μ and measured from bands of the spectrum of water vapour. Mechanical reproducibility of the instrument is ± 0.007μ, with precision in estimating peak frequency, depending on width of absorption band, approximately 0.005 to 0.03μ.

The other figures obtained from spectra run at 5 cm = 1μ with water vapour spectrum reference. The precision in estimating peak frequency is 0.02 to 0.04μ.

TABLE 12

Frequencies (cm^{-1}) and assignments for NH_4^+

Salt	Assignment (Waddington, 1958) ν_4 (N-H deformation)	$\nu_4 + \nu_6$	$2\nu_4$	$\nu_2 + \nu_4$	ν_3 (N-H stretch)
NH_4Br	1401 (1429)	1712	2833	3031	3137
NH_4Cl	1403 (1445)	1762	2870	3044	3138
NH_4Cl*	1408,1418 (1445)	1751	2808	3049	3145
NH_4Cl* (aq. solution)	1449	-	2882	-	3058(a)
NH_4F	1484 (1503)	2007	2830	3024	3100
NH_4N_3	1414	1810	2830	3000	3140
NH_4NO_3	1420 (1455)	1765	2860	3100	3160
NH_4BF_4	1431	-	-	-	3332
NH_4^+ montmorillonite	1411	-	-	3040	3193(a)

* present work

(a) partially obscured by OH of water or clay

( ) weaker shoulder

Waddington gives the N-H stretching frequency (ν_3) for an unassociated ammonium ion as 3332 cm^{-1} (NH_4BF_4) to 3222 cm^{-1} (NH_4BPh_4). The depression of some 29 to 139 cm^{-1} in ν_3 for ammonium montmorillonite suggests that a hydrogen bond weaker than that present in NH_4Br or NH_4Cl may be present in the adsorbed phase. However, the absence of the combination band $\nu_4 + \nu_6$ and the absence of a splitting of the degeneracy of ν_4, indicate that the ammonium ion in the adsorbed phase is free to rotate. Free rotation of the ammonium ion is not possible if there is significant bond formation between the ions and the surface oxygens. The depression in ν_3 for ammonium montmorillonite is therefore due to an interaction of the hydrogen bonding type with too low an energy to constitute true bond formation at ordinary temperatures.

(ii) The spectra of tetraalkylammonium ions and their complexes with montmorillonite

a. Tetramethylammonium

The close agreement of the spectrum of the aqueous solution of Me_4NBr with that of the adsorbed phase cation in the C-H deformation region (Table 13) indicates that there is no significant change in the conformation of the cation on intercalation by montmorillonite. There is a doubling and depression of the 1400 cm^{-1} band on passing to the solid phase of Me_4NBr which may be attributed to electrostatic interactions within the crystal.

b. Tetraethylammonium

The infra-red spectrum of Et_4N^+ in tetraethylammonium montmorillonite supports the flatter conformation of the intercalated cation given by Barrer and MacLeod (1955). Again, a comparison of the spectrum of the adsorbed phase cation with that of the cation in aqueous solution of Et_4NBr indicates no further alteration in the conformation of the cation on intercalation.

c. Tetrapropyl- and tetrabutylammonium

The correlations given in Table 11 show no evidence of compressive or crystal influences on the conformations of these two cations on intercalation. The spectrum and basal spacing of tetrapropylammonium montmorillonite both indicate that the intercalated cation is flattened on the clay surface. There are a number of possible conformations of the tetrabutylammonium ion that will fit the basal spacing of the corresponding montmorillonite [d(001) = 16.3 Å].

The infra-red spectrum has absorptions corresponding to methylene scissoring modes in the strained conformation (1486 cm^{-1}) and the unstrained conformation (1464 cm^{-1}). Again, a number of ionic conformations will satisfy these data.

It may be concluded that in regard to adsorption energetics the infra-red spectra of intercalated tetraalkylammonium ions yield no evidence to suggest that the conformations of the cations are influenced by compressive or crystal effects. In particular, the apparent contraction in the van der Waals thickness of the ions on intercalation is not due to their compression.

TABLE 13

Frequencies and assignments for tetramethyl- and tetraethylammonium in aqueous solution and in the adsorbed phase, C-H deformation region.

Cation	Frequency (cm^{-1})		Assignment
	Adsorbed phase	Aqueous solution	
Me_4N^+	1491 (s,sp)	1488 (s,sp)	Asymmetric C-H deformation
	1420 (w)	1419 (vw)	Symmetric C-H deformation plus ν_3 of the NC_4 tetrahedron
Et_4N^+	1494 (s,sp)	1488 (s)	CH_2 scissor, flat conformation
		1475 (sh)	Asymmetric C-H deformation, methyl
	1463 (w)*	1459 (m)	CH_2 scissor, tetrahedral conformation
	1446 (w)	1444 (sh)	Asymmetric C-H deformation, methyl
		1407 (vwsh)	ν_3 of the N-C_4 skeleton
	1398 (s)	1397 (s)	
	1376 (w)	1368 (w)	Symmetric C-H deformation, methyl

* The presence of tetrahedral conformation in the methyl. adsorbed phase is attributed to adsorption on the external surfaces. This band is absent in the spectrum of tetraethylammonium vermiculite which has a very much lower external surface area.

v = weak; s = strong; sh = shoulder; sp = sharp; m = medium; w = weak.

CHAPTER IV.

THE SWELLING OF COMPLEXES BETWEEN MONTMORILLONITE AND ALKYLAMMONIUM COMPOUNDS

IV. 1. Introduction

A number of long chain quaternary ammonium and alkylpyridinium compounds have been shown to be effective in controlling and reducing the water uptake and swelling of soils and clays (Clare, 1947; Emerson, 1960) and in increasing the water-stability and mechanical strength of soil aggregates (Grossi and Woolsey, 1955). Emerson (1962) reported that the addition of about 3 milliequivalent cetyltrimethylammonium bromide (CTAB) per 100 g of clay effectively reduced the expansion of Ca^{++} montmorillonite flakes when immersed in dilute $CaCl_2$ solutions and distilled water. It was proposed that the CTA^+ ions were adsorbed on the external crystal surface of the clay. This prevented the formation of diffuse double layers between crystals and hence intercrystalline swelling was reduced.

Recent studies by Posner and Quirk (1963) on the adsorption of water from strong electrolyte solutions by montmorillonite and illite have led to the conclusion that surface adsorption of water by the exchangeable cations provides the trigger mechanism for the formation of a gel structure. It is expected that the replacement of the exchangeable cations by alkylammonium cations will modify surface adsorption which gives rise to particle re-arrangement and the creation of a gel structure. The introduction of increasing amounts of alkylammonium cations into the exchange complex is thought to disrupt the water structures associated with the exchangeable cations and hence modify the electrostatic attractive forces which influence the crystalline swelling of montmorillonite.

The present study aims to clarify the mechanism by which organic cations modify the swelling of clays by relating the uptake and retention of water under controlled conditions and at different hydrostatic suctions to the crystalline swelling observed by X-ray diffraction methods (Chapter III) and to adsorption mechanisms (Chapter II).

IV. 2. Experimental

All swelling measurements were carried out in a constant temperature room, maintained at 20 ± 0.2 °C.

IV. 2. 1. Description of the principal apparatus used

a. The suction plate (Aylmore, 1960)

This apparatus was used to obtain water contents of clays in the range of hydrostatic suctions between 1 and 700 cm, corresponding to pF 0 and pF 2.8, respectively. The apparatus consists of a porous ceramic plate mounted in perspex and provided with a reservoir of water underneath which is connected to a cylindrical flask. A constant small head of water can be maintained in the flask which can be disconnected from the reservoir by closing the tap. The dome-like perspex lid is sealed to the base by means of a number of srews. A rubber "O" ring between lid and base ensures freedom from leaks of gas to the atmosphere. An opening in the lid is connected to a lead from the water towers where a desired constant head of water is maintained by bubbling nitrogen gas from a cylinder.

b. The pressure membrane apparatus

This apparatus was used to determine the water content of cores at pF 4.2 corresponding to a hydrostatic suction of 15 atmospheres. In principle, the construction is similar to the original model described by Richards (1947) except that the flat rubber gaskets were replaced by rubber "O" rings. Nitrogen gas from a cylinder was introduced into the compartment above the membrane at a pressure of 224 lbs per square inch (15 atmospheres). A "Visking" cellophane membrane was used which was immersed in distilled water for 24 hours before use. The reservoir below the membrane is connected to a cylindrical flask containing water. The cores were allowed to equilibrate for a period of 4 days or longer.

c. The constant humidity desiccator

A saturated solution of a salt placed in a glass bowl in the bottom of a vacuum desiccator maintains an atmosphere of constant relative humidity (P/P_o) in the space above it. To maintain a steady vacuum condition the desiccator was evacuated with a water pump at weekly intervals. Equilibrium was attained within one week but cores were kept for at least 10 days before they were taken out, weighed and dried in the oven at 105°C overnight.

Values of relative humidity at 20°C for the different salt solutions used and equivalent pF values are summarized in Table 14.

TABLE 14

Relative humidity of saturated salt solutions at 20°C and equivalent pF value.

Salt solution	P/P_o	pF*
K_2SO_4	0.96	4.68
KCl	0.86	5.32
NaCl	0.75	5.58
$Ca(NO_3)_2$	0.51	5.97
$MgCl_2$	0.33	6.18
$CaBr_2$	0.19	6.36
LiCl	0.15	6.42

* pF values were calculated from the formula (Schofield, 1935)

$$pF = 6.5 + \log_{10}(2 - \log_{10} P/P_o)$$

IV. 2. 2. Methods

The complexes between montmorillonite and alkylammonium compounds were prepared by adding standard solutions of the compounds to air-dry clay, shaking and centrifuging the suspension.

After decanting the supernatant solution the centrifuged material was washed three times with distilled water to remove excess electrolyte. This procedure did not remove the organic cations present on the clay since the amount adsorbed before and after washing with water remained unaltered. The washed material was dried in an electric oven at 70°C and ground to pass a 60 mesh sieve. The air-dry powder was placed in a vacuum desiccator over saturated K_2SO_4 solution ($P/P_o = 0.96$) for a period of 5 days or longer. Cores were manufactured from the moist powder by the method of Aylmore and Quirk (1959, 1960b). The cores were wet in stages of pF 2.8 → 2.0 → 1.1 on suction plates. A complete drying cycle was obtained by taking the cores wet at pF 1.1 through stages of pF 2.0 → 2.8 → 4.2 (pressure membrane) and subsequently through constant humidity desiccators (pF 4.68 - pF 6.42) and finally to complete desiccation over P_2O_5. The wetting cycle was determined by taking the cores dried over P_2O_5 through the same sequence in reverse order. Aylmore (1960) has shown that for montmorillonite saturated with inorganic cations, differences in the amounts of water adsorbed or retained at different pF's between the first and subsequent wetting-drying cycles were slight. The water contents reported in this work were obtained from cores which were submitted to the following cycle of wetting and drying: cores initially wet at 96 per cent relative humidity were dried over P_2O_5 and then allowed to take up water in stages up to pF 1.1 and subsequently submitted to a drying cycle up to pF 6.42.

The rate of wetting and the time required for Na^+ and Ca^{++} montmorillonite cores to reach equilibrium at pF 2.8, pF 2.0 and pF 1.1 were determined in a preliminary investigation. The results of this study are shown in Figure 19. Further adsorption of water after 14 days from the time the cores were transferred from pF 2.8 to pF 2.0 and from the latter to pF 1.1, was very slight. An equilibrium time of 14 days or longer was therefore adopted for each pF. The results were reproducible and differences in water content between duplicate cores were less than two per cent.

Figure 19.

Approach to equilibrium for cores of sodium and calcium montmorillonite at hydrostatic suction of 700 cm (pF 2.8), 100 cm (pF 2.0), and 15 cm (pF 1.1).

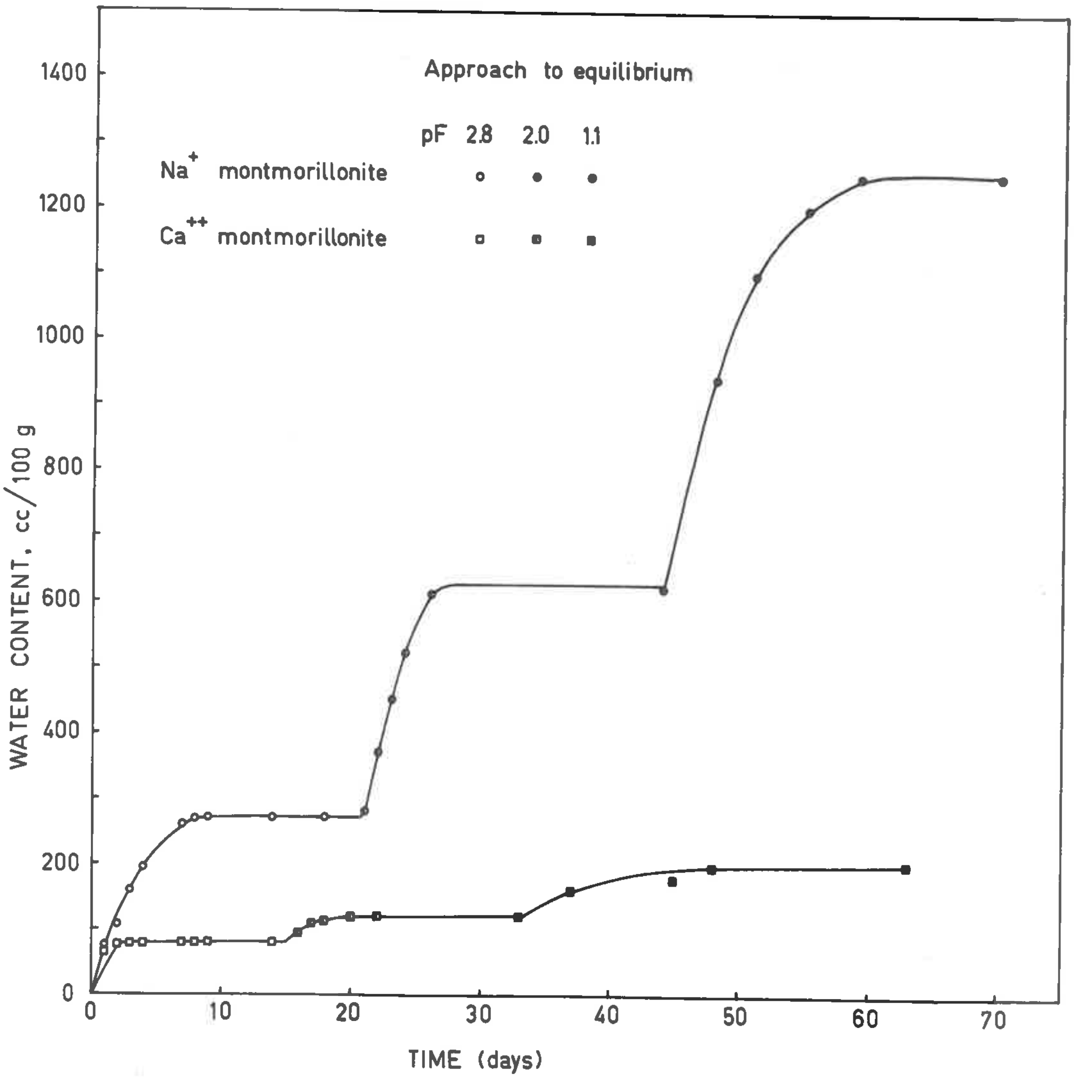

Approach to equilibrium
pF 2.8 2.0 1.1
Na$^+$ montmorillonite ○ ● ●
Ca^{++} montmorillonite □ ■ ■
WATER CONTENT, cc/100 g
0
200
400
600
800
1000
1200
1400
TIME (days)
0
10
20
30
40
50
60
70

Figure 19

IV. 3. Results

(i) Na^+ montmorillonite

The water contents of cores in equilibrium with a hydrostatic suction of 15 cm (pF 1.1) for Na^+ montmorillonite containing different amounts of alkylammonium cations are plotted against the fraction of surface covered by the organic cations (Figures 20 to 24). Surface coverage at any given amount adsorbed refers to Θ_r calculated on the assumption that the cation occupied an area given by the smallest containing rectangle which can be described around the projection of the cation on a planar surface (see III. 3.). For triethylammonium Θ_p was chosen for reason of its triangular shape.

Plots similar to those shown in Figures 20 to 24 were obtained at hydrostatic suctions of 100 cm (pF 2.0) and 700 cm (pF 2.8). The water contents of complexes at pF 2.0 and pF 2.8 are presented in Appendix VII.

Water content is expressed as the volume of water adsorbed or retained per 100 g of ovendry (105°C overnight) clay free of organic material. Complete water content-pF relationships for the drying and wetting cycles of fully saturated complexes with alkylammonium cations are presented in Figures 25 to 27.

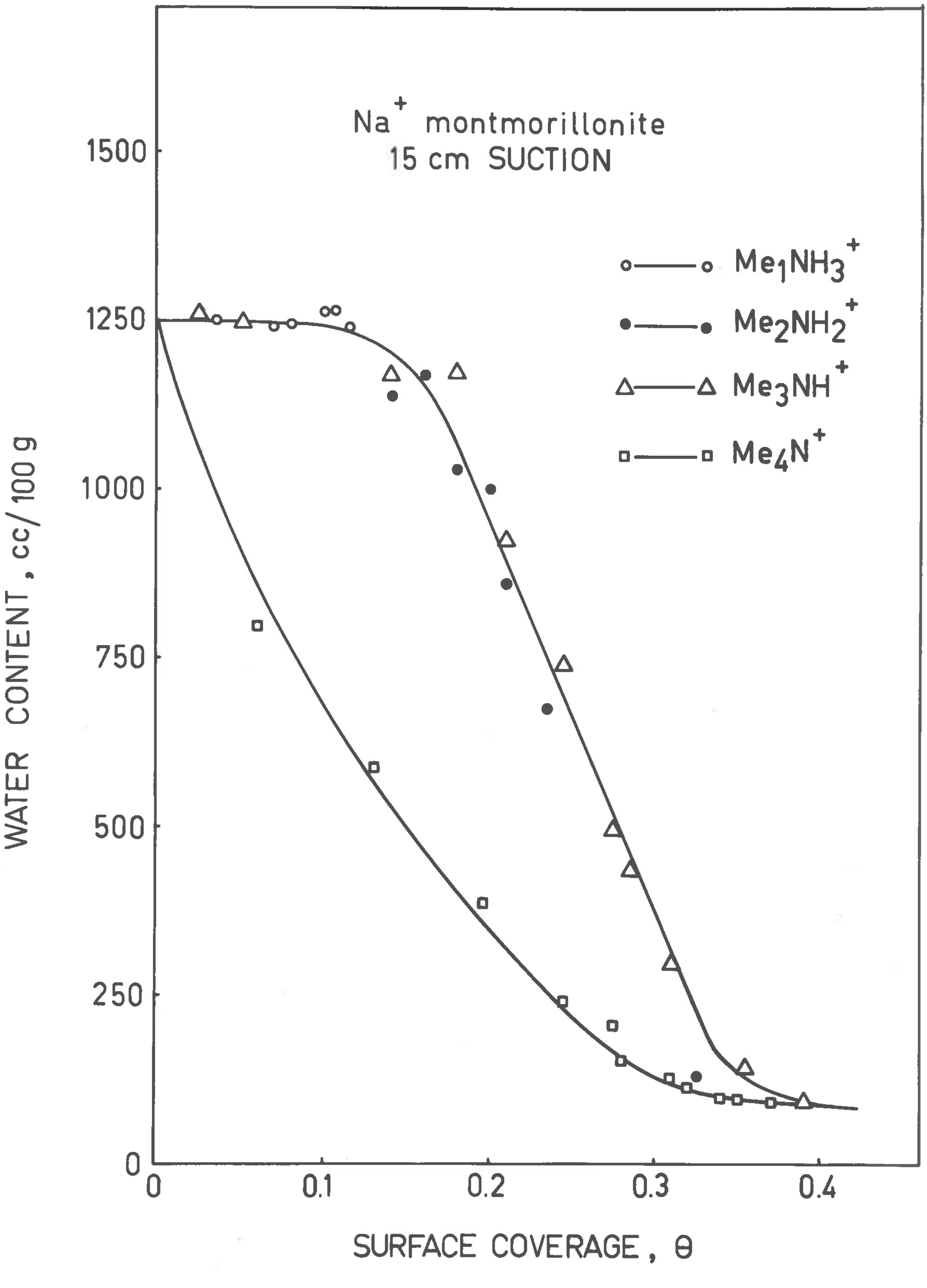
Water vapour sorption isotherms at 20°C for Na^+ montmorillonite and complexes partially and fully saturated with alkylammonium cations are shown in Figures 28 to 30.

(ii) Ca^{++} montmorillonite

The water content of cores at pF 1.1 containing different amounts of monovalent inorganic and alkylammonium cations is plotted

Figure 20.

Water content on wetting to pF 1.1 of Na^+ montmorillonite cores as a function of surface coverage by methyl-substituted ammonium cations. Surface coverage in figure refers to θ_r.



Na^+ montmorillonite
15 cm SUCTION
$Me_1NH_3^+$
$Me_2NH_2^+$
Me_3NH^+
Me_4N^+
WATER CONTENT, cc/100 g
0
250
500
750
1000
1250
1500
SURFACE COVERAGE, θ
0
0.1
0.2
0.3
0.4

Figure 20

Figure 21.

Water content on wetting to pF 1.1 of Na^+ montmorillonite cores as a function of surface coverage by ethyl-substituted ammonium cations. Surface coverage in figure refers to θ_r except for triethylammonium where θ_p was chosen.

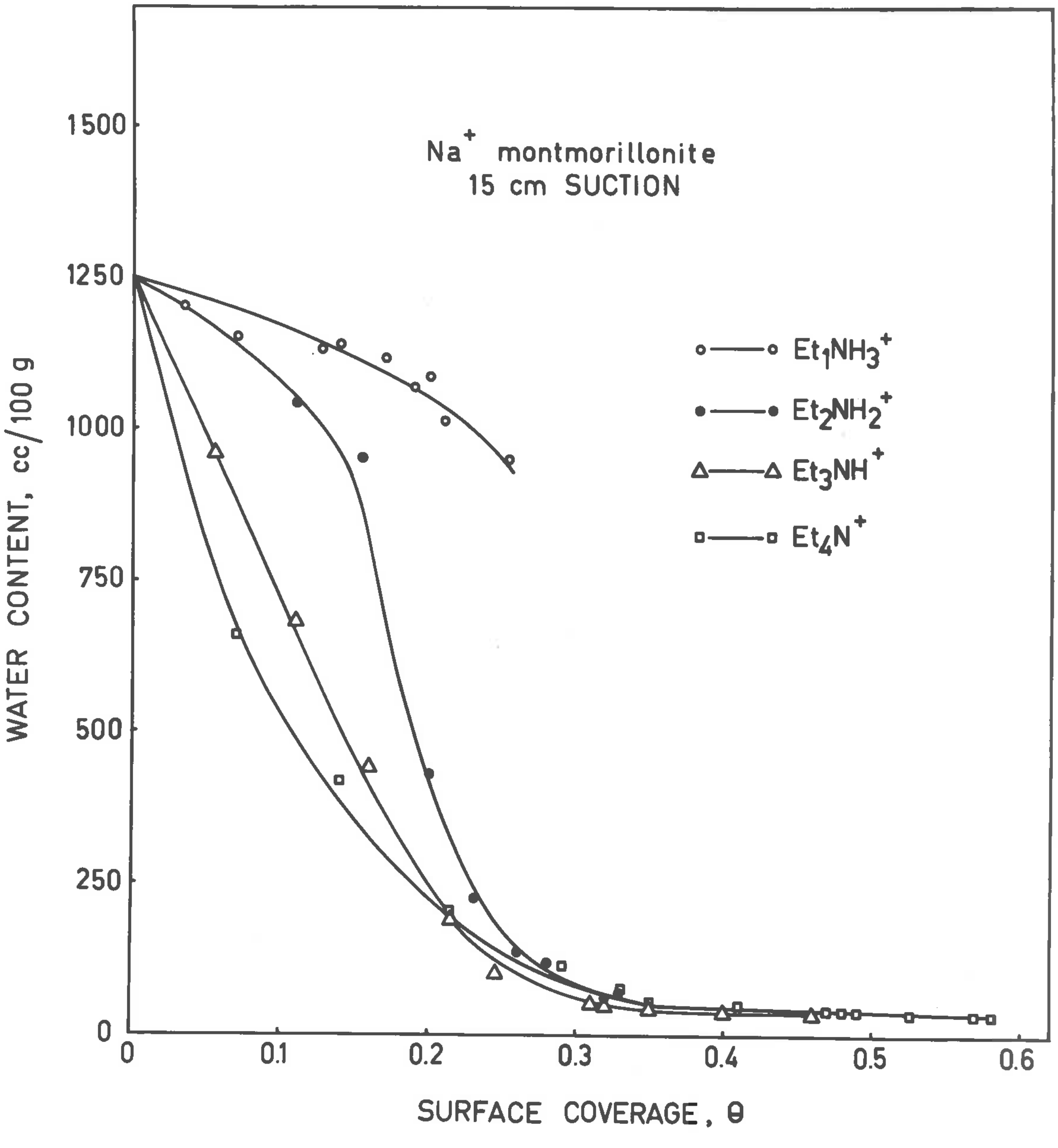

Na$^+$ montmorillonite
15 cm SUCTION
$Et_1NH_3^+$
$Et_2NH_2^+$
Et_3NH^+
Et_4N^+
WATER CONTENT, cc/100 g
1500
1250
1000
750
500
250
0
SURFACE COVERAGE, θ
0
0.1
0.2
0.3
0.4
0.5
0.6

Figure 21

Figure 22.

Water content on wetting to pF 1.1 of Na^+ montmorillonite cores as a function of surface coverage by propyl-substituted ammonium cations. Surface coverage in figure refers to θ_r.

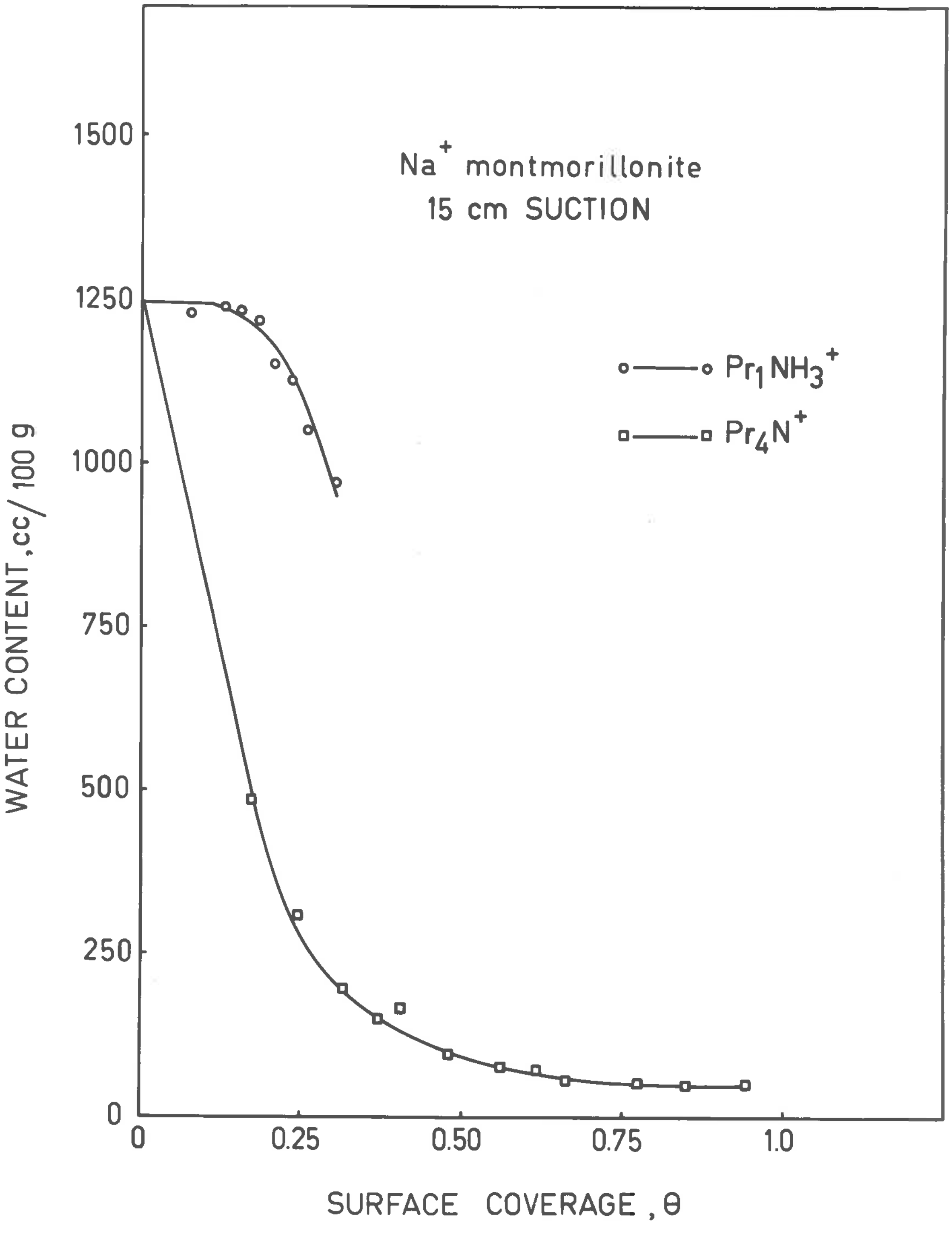

Na$^+$ montmorillonite
15 cm SUCTION
$Pr_1NH_3^+$
Pr_4N^+
WATER CONTENT, cc/100 g
1500
1250
1000
750
500
250
0
0
0.25
0.50
0.75
1.0
SURFACE COVERAGE, θ

Figure 22

Figure 23.

Water content on wetting to pF 1.1 of Na^+ montmorillonite cores as a function of surface coverage by butyl-substituted ammonium cations. Surface coverage in figure refers to θ_r except for tetrabutylammonium where θ_p was chosen.

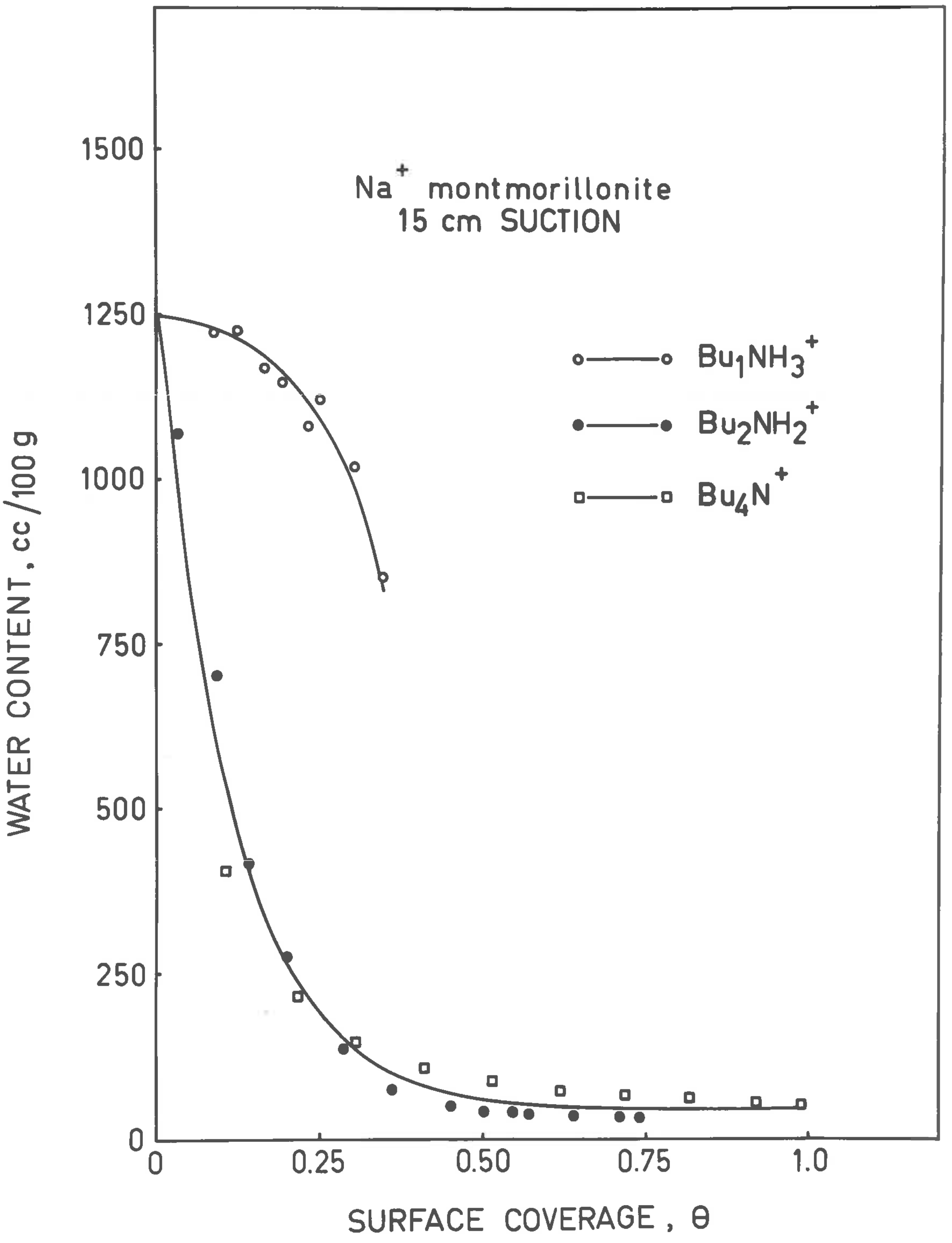

Na$^+$ montmorillonite
15 cm SUCTION
Bu$_1$NH$_3^+$
Bu$_2$NH$_2^+$
Bu$_4$N$^+$
WATER CONTENT, cc/100 g
1500
1250
1000
750
500
250
0
0
0.25
0.50
0.75
1.0
SURFACE COVERAGE, θ

Figure 23

Figure 24.

Water content on wetting to pF 1.1 for Na^+ montmorillonite cores as a function of surface coverage by tetraalkylammonium cations. Surface coverage refers to θ_r except for tetrabutylammonium where θ_p was chosen.

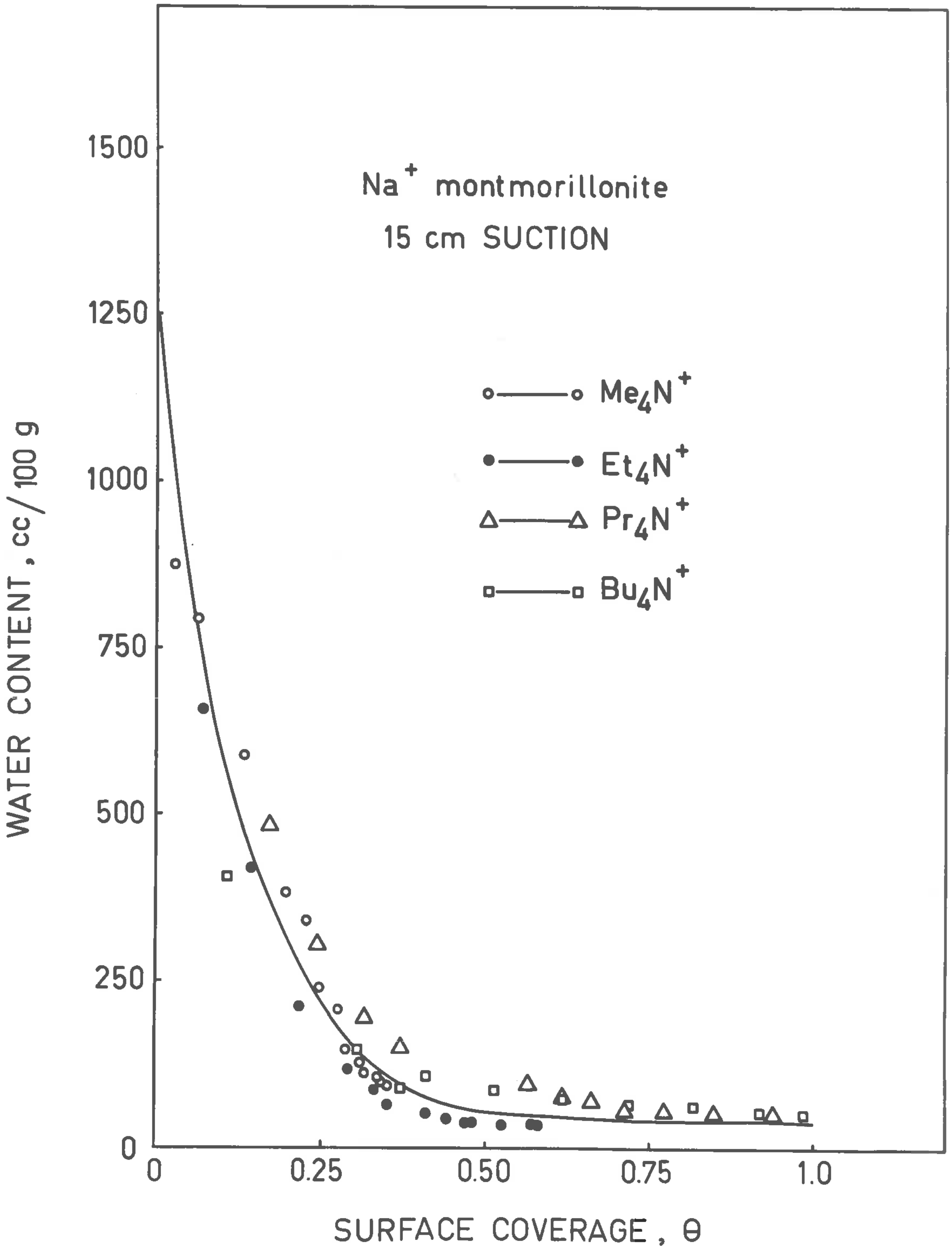
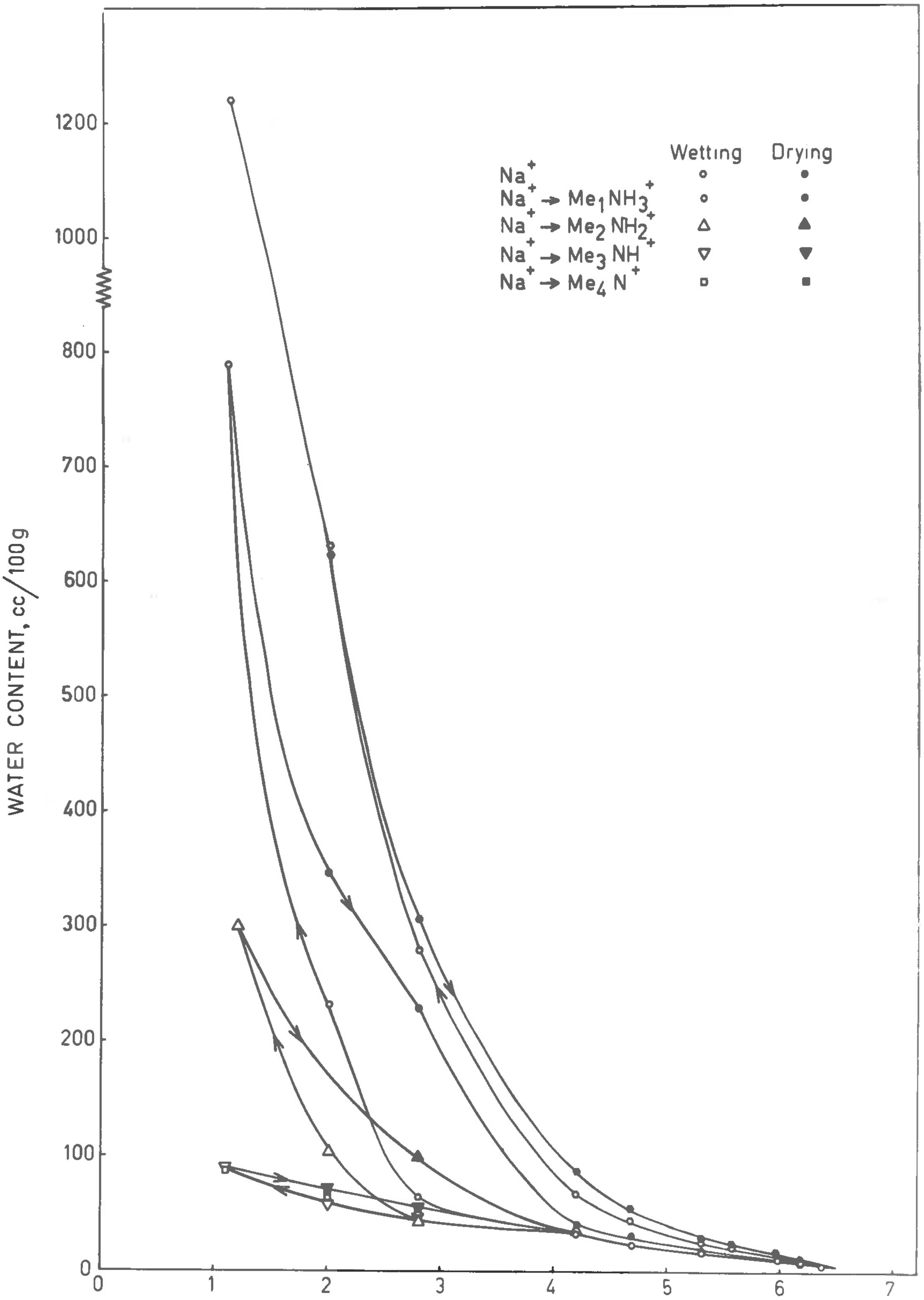

Na⁺ montmorillonite
15 cm SUCTION
Me₄N⁺
Et₄N⁺
Pr₄N⁺
Bu₄N⁺
WATER CONTENT, cc/100 g
1500
1250
1000
750
500
250
0
0
0.25
0.50
0.75
1.0
SURFACE COVERAGE, θ

Figure 24

Figure 25.

Water content - pF relationship for cores of Na^+ montmorillonite and its complexes saturated with methyl-substituted ammonium cations.



WATER CONTENT, cc/100g
1200
1000
800
700
600
500
400
300
200
100
0
0
1
2
3
4
5
6
7
pF
Wetting
Drying
Na+ ○ ●
Na+ → Me1NH3+ ○ ●
Na+ → Me2NH2+ △ ▲
Na+ → Me3NH+ ▽ ▼
Na+ → Me4N+ ▫ ▪

Figure 25

Figure 26.

Water content - pF relationship for cores and complexes saturated with ethyl-substituted ammonium cations.

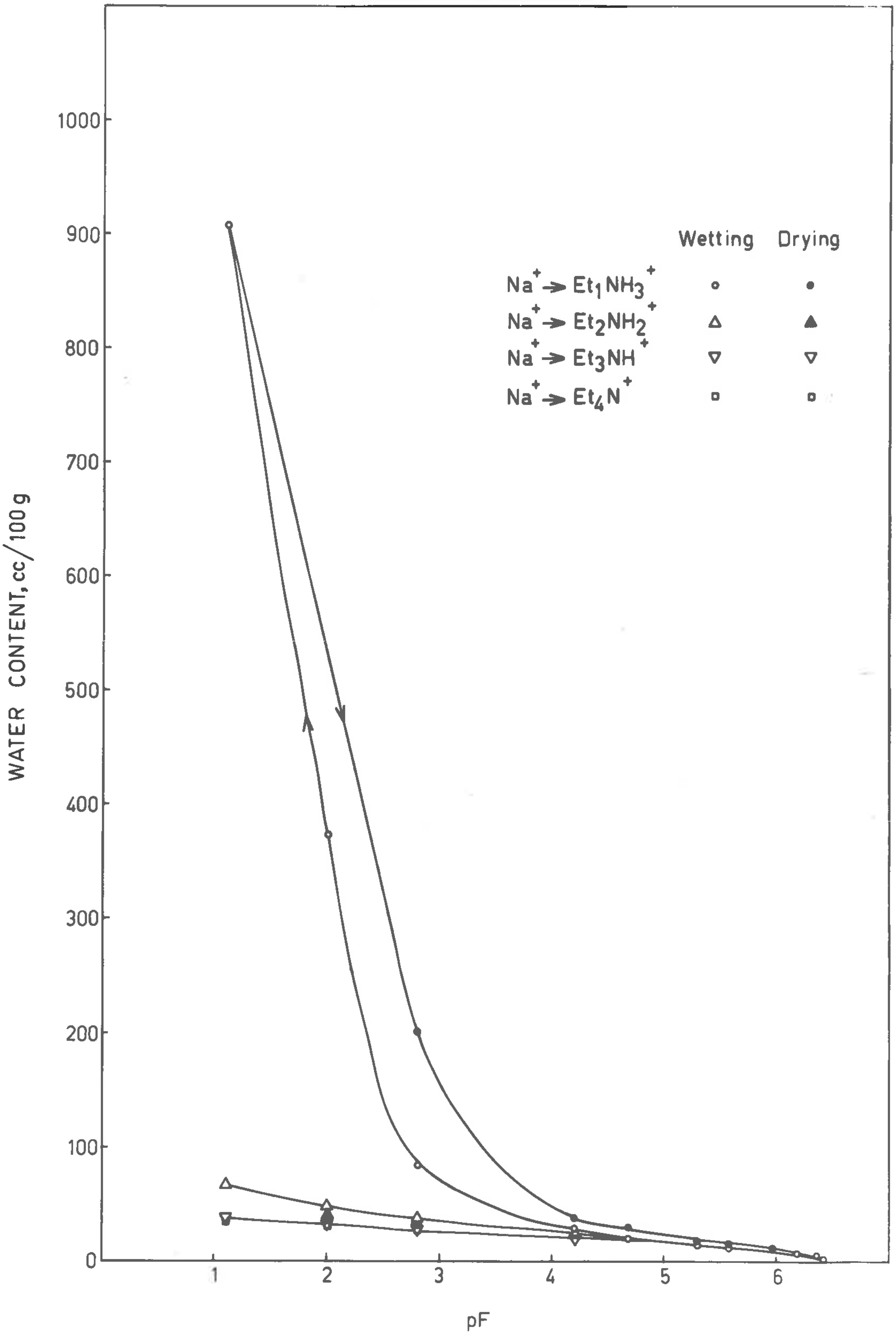
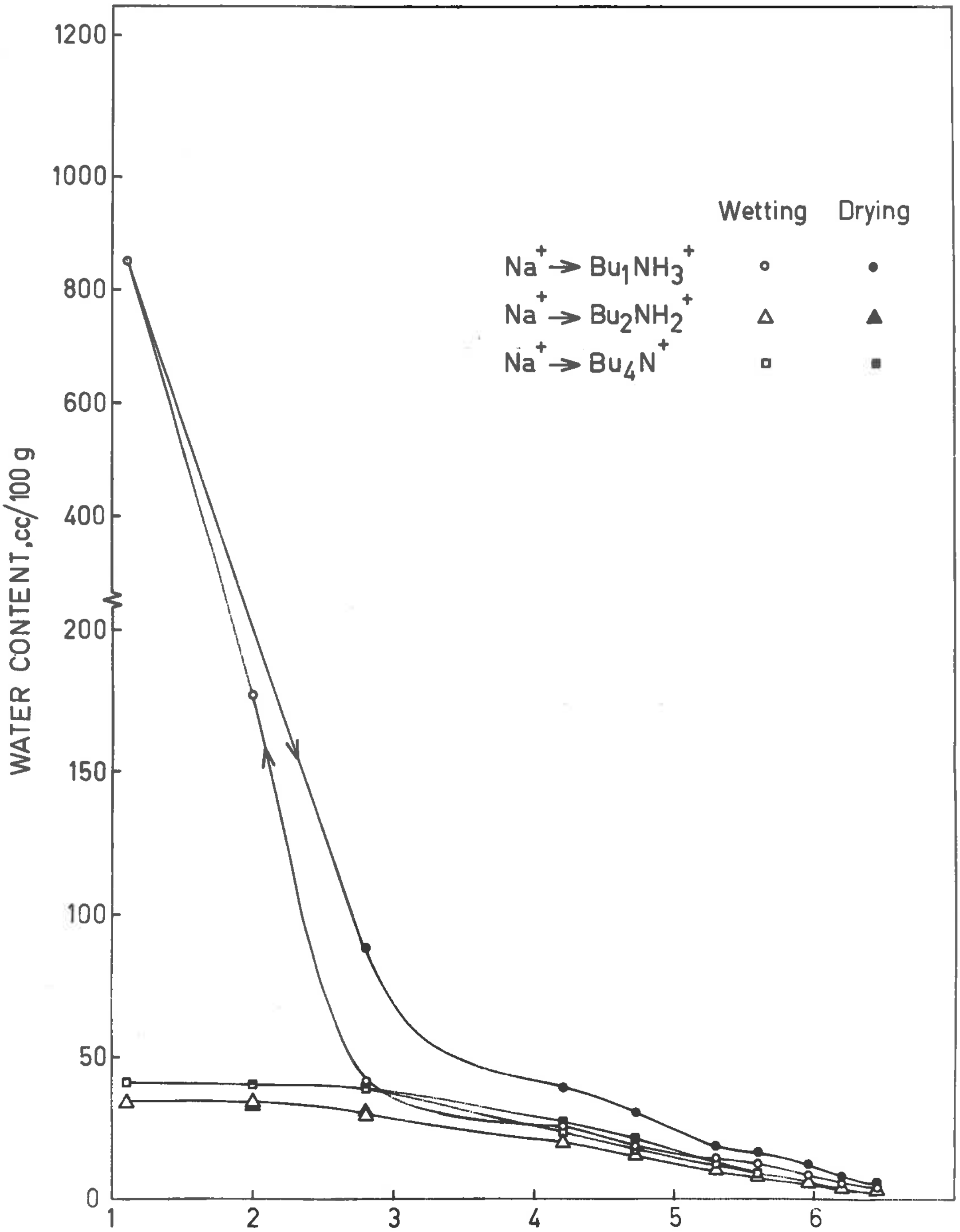

WATER CONTENT, cc/100 g
pF
0
100
200
300
400
500
600
700
800
900
1000
1
2
3
4
5
6
Wetting
Drying
Na⁺ → Et₁NH₃⁺ ○ ●
Na⁺ → Et₂NH₂⁺ △ ▲
Na⁺ → Et₃NH⁺ ▽ ▽
Na⁺ → Et₄N⁺ □ □

Figure 26

Figure 27.

Water content-pF relationship for cores of complexes saturated with butyl-substituted ammonium cations.



WATER CONTENT, cc/100 g
1200
1000
800
600
400
200
150
100
50
0
pF
1
2
3
4
5
6
Wetting
Drying
Na⁺ → Bu₁NH₃⁺ ○ ●
Na⁺ → Bu₂NH₂⁺ △ ▲
Na⁺ → Bu₄N⁺ □ ■

Figure 27

Figure 28.

Water vapour sorption isotherms at 20 °C for cores of Na^+ montmorillonite and its complexes containing different amounts of monoethylammonium cations.

Relative humidity in per cent.

No.	Amount adsorbed, (me/100 g)
(5)	17.3
(8)	41.9
(12)	75.8

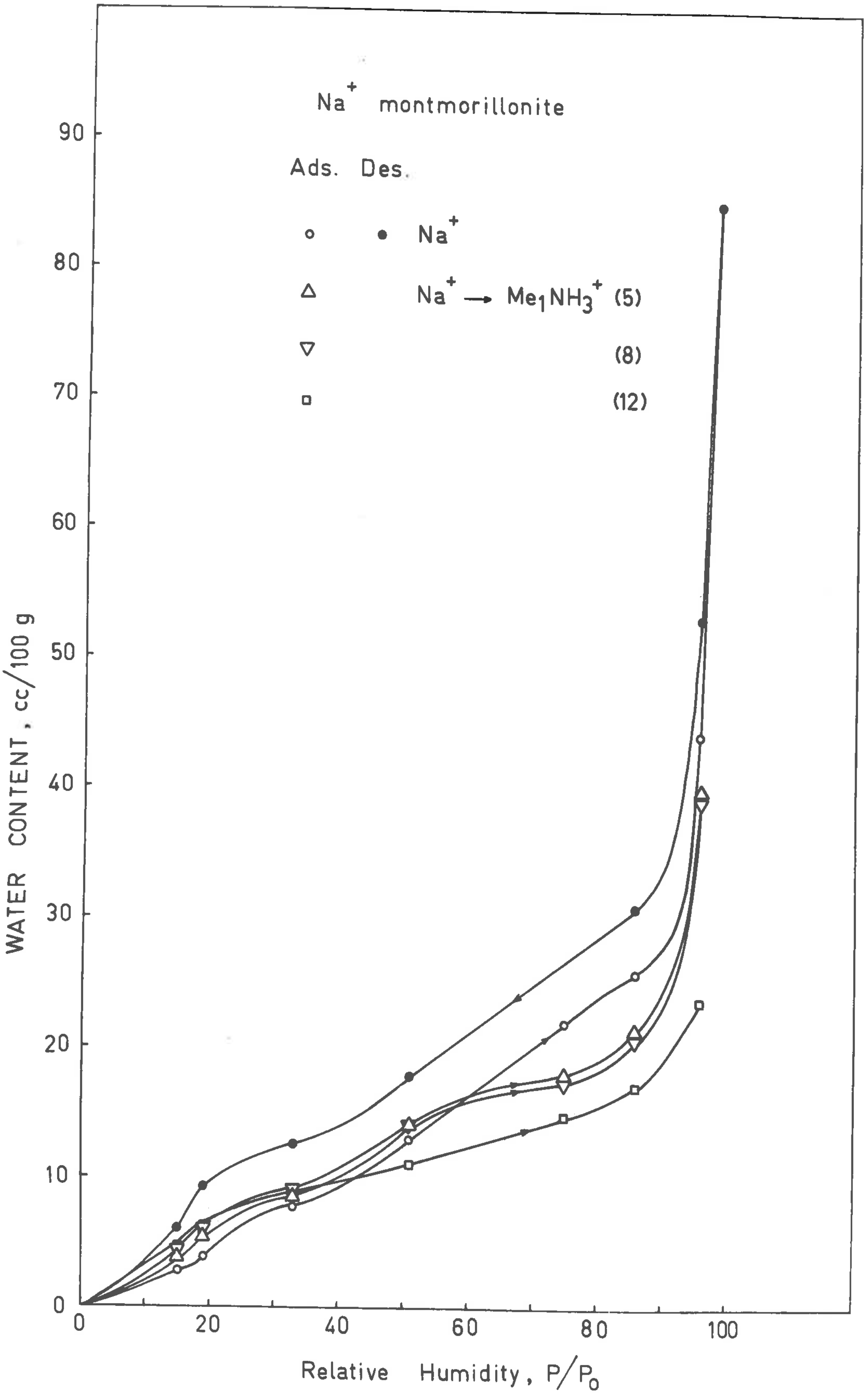

Na$^+$ montmorillonite
Ads. Des.
○ ● Na$^+$
△ Na$^+$ → Me$_1$NH$_3^+$ (5)
▽ (8)
□ (12)
WATER CONTENT, cc/100 g
0
10
20
30
40
50
60
70
80
90
0
20
40
60
80
100
Relative Humidity, P/P$_0$

Figure 28

Figure 29.

Water vapour sorption isotherms at 20 °C for cores of Na^+ montmorillonite and its complexes saturated with monomethyl-, monoethyl-, and mono-n-butylammonium cations. Relative humidity in per cent.

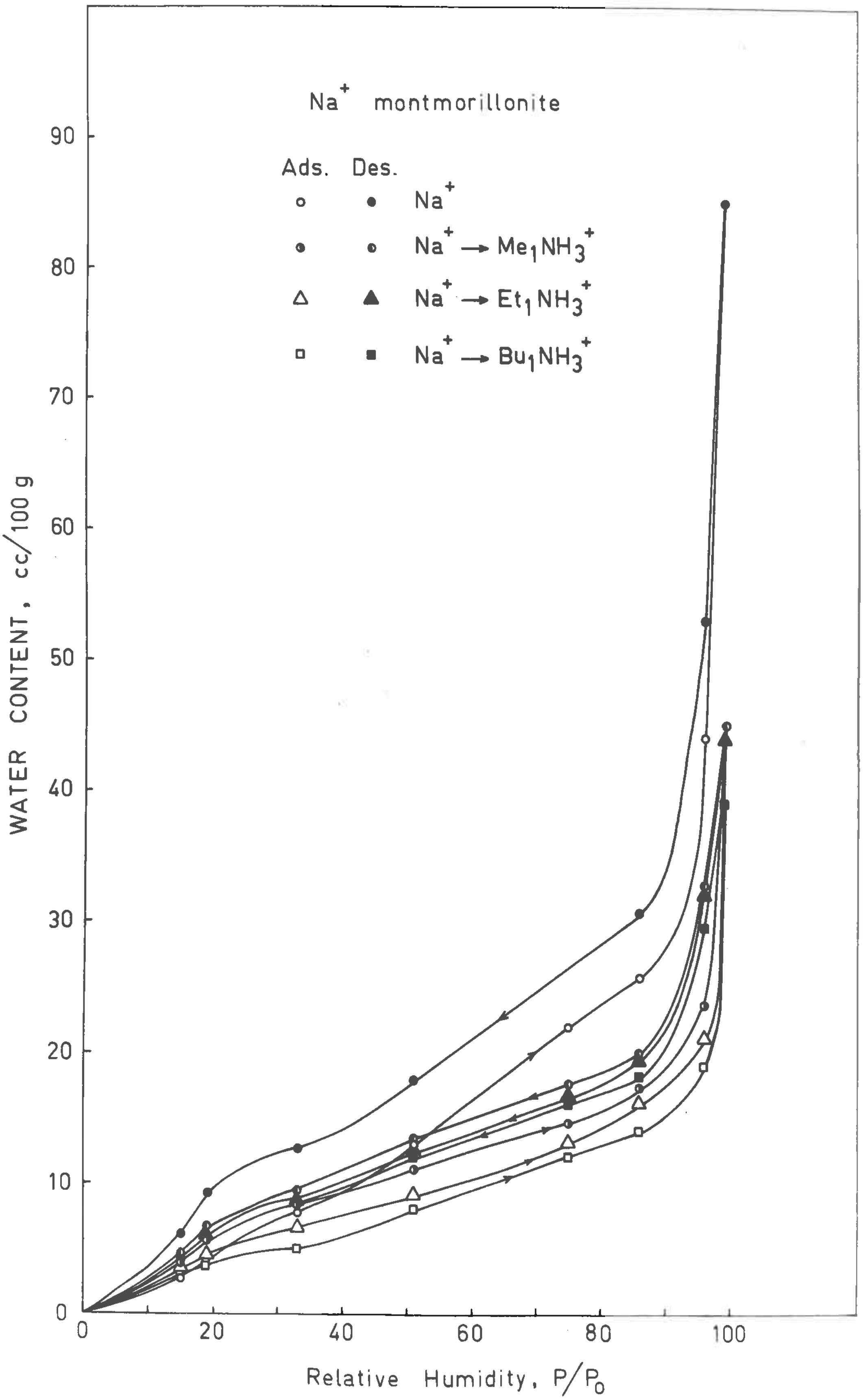

Na$^+$ montmorillonite
Ads. Des.
○ ● Na$^+$
Na$^+$ → Me$_1$NH$_3^+$
△ ▲ Na$^+$ → Et$_1$NH$_3^+$
□ ■ Na$^+$ → Bu$_1$NH$_3^+$
WATER CONTENT, cc/100 g
0
10
20
30
40
50
60
70
80
90
0
20
40
60
80
100
Relative Humidity, P/P$_0$

Figure 29

Figure 30.

Water vapour sorption isotherms at 20 °C for cores of complexes saturated with triethylammonium, tetraethyl-, tetra-n-propyl-, and tetra-n-butylammonium cations. Relative humidity in per cent.

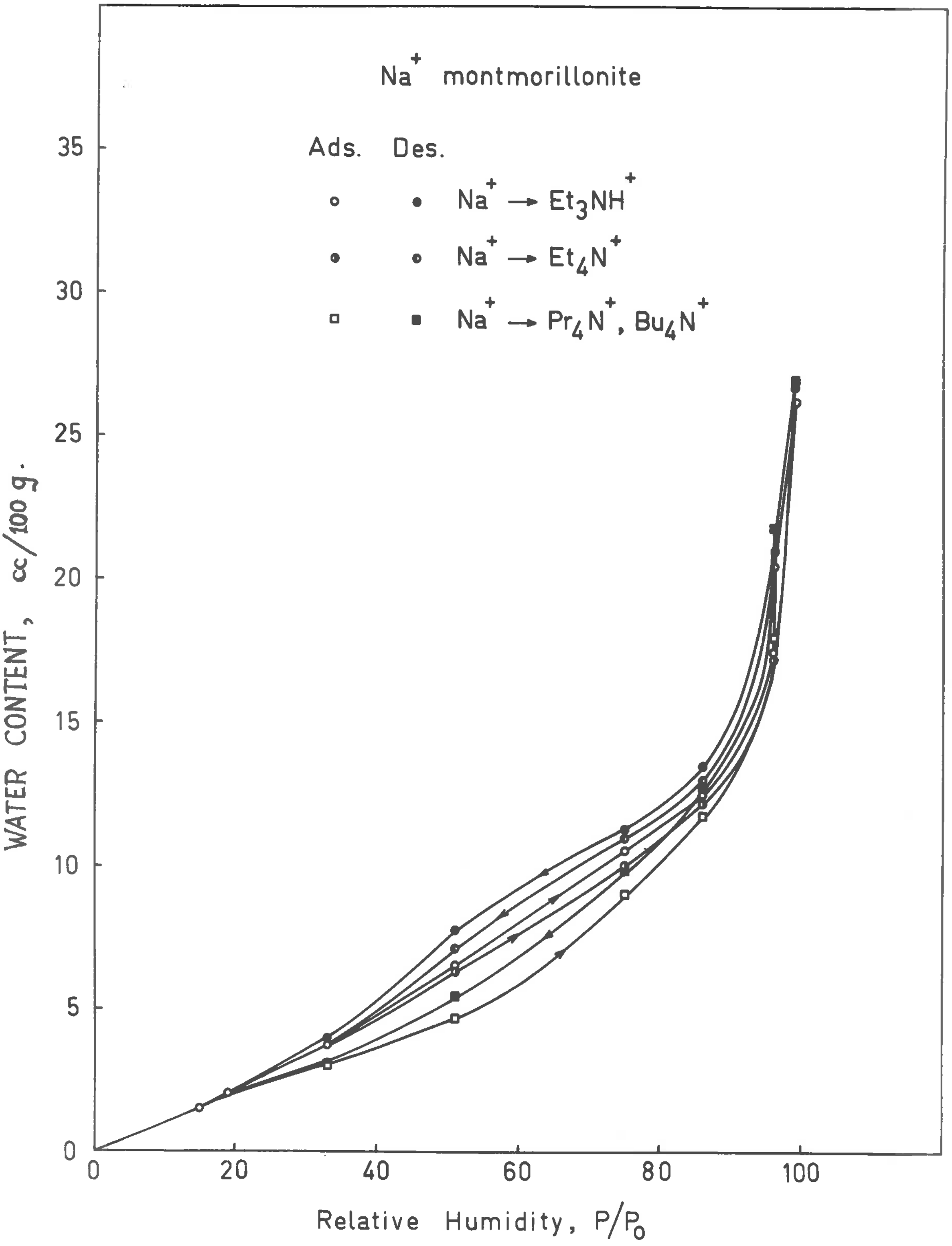

Na+ montmorillonite
Ads. Des.
○ ● Na+ → Et3NH+
◉ ◉ Na+ → Et4N+
□ ■ Na+ → Pr4N+, Bu4N+
WATER CONTENT, cc/100 g.
0
5
10
15
20
25
30
35
0
20
40
60
80
100
Relative Humidity, P/Po

Figure 30

in Figures 31 to 34. The amounts of water taken up at pF 2.0 and at pF 2.8 by the complexes are summarized in Appendix VII.

Water vapour sorption isotherms at 20°C for Ca^{++} montmorillonite and for complexes containing different amounts of alkylammonium cations are shown in Figures 35 and 36.

IV. 4. Discussion

The variation in the amount of water adsorbed or retained by complexes as a function of surface coverage or degree of saturation by the alkylammonium ions at different values of pF or relative humidity was essentially different for Na^+-alkylammonium complexes than for Ca^{++}-alkylammonium complexes. For this reason the results will be discussed under separate headings.

IV. 4. 1. Na^+ montmorillonite.

(i) Water uptake and retention in the range of pF 2.8 to pF 1.1

Figures 20 to 24 show that the amount of water adsorbed at pF 1.1 decreased in a regular fashion with an increase in surface coverage. For a given surface coverage, θ_r, the effectiveness of a given cation in reducing water uptake increased with the size of the organic cation. Since the crystalline swelling of fully saturated complexes was limited much of the reduction in the amount of water retained was due to a reduction of water held in the interlamellar region by the collapse of diffuse double layers. This collapse is expected to occur in those regions within a crystal which were predominantly saturated with alkylammonium cations since the exchange of Na^+ for alkylammonium ions appeared to occur in discrete layers

Figure 31.

Water content on wetting to pF 1.1 of Ca^{++} montmorillonite cores as a function of the amount of monoalkylammonium cations adsorbed.

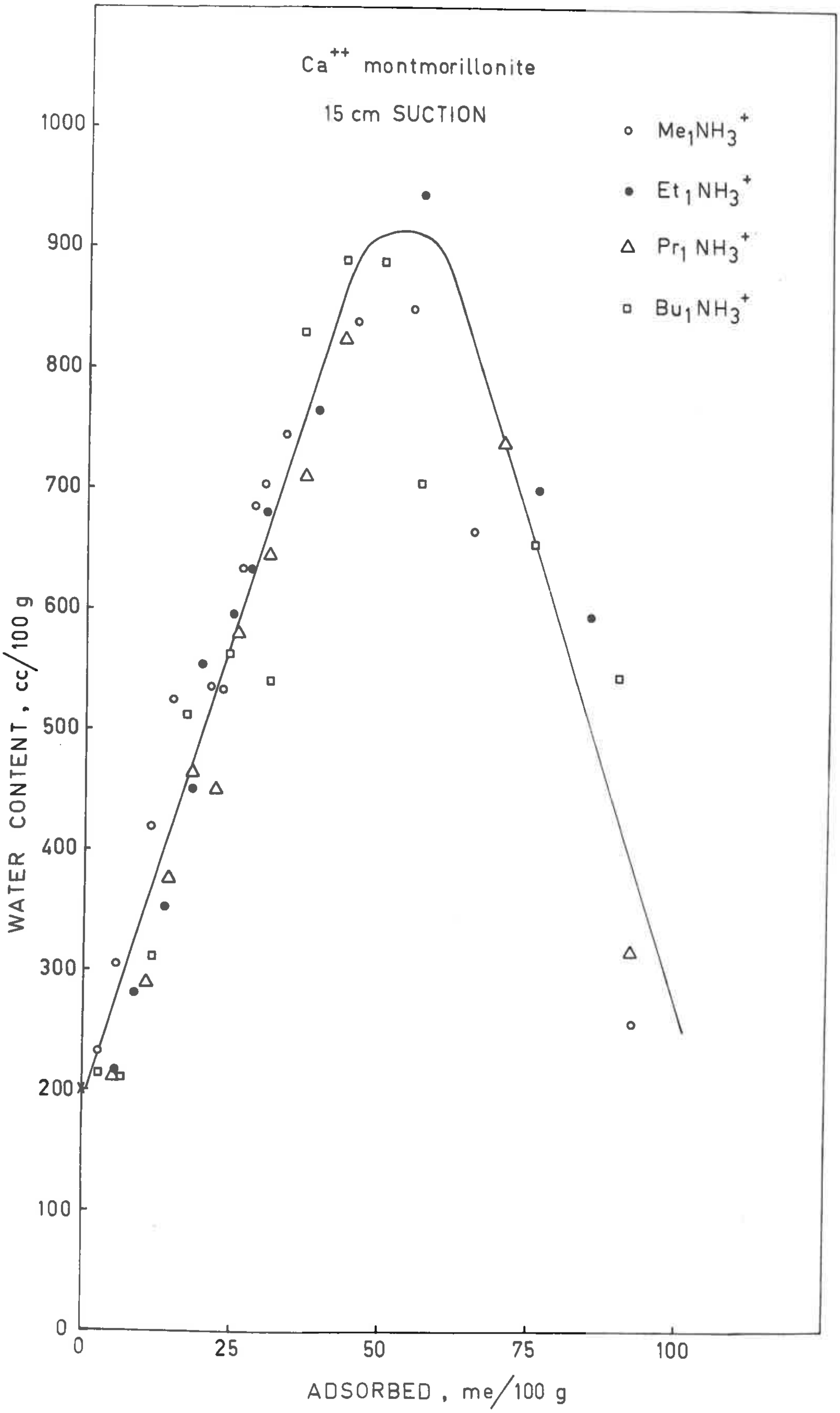
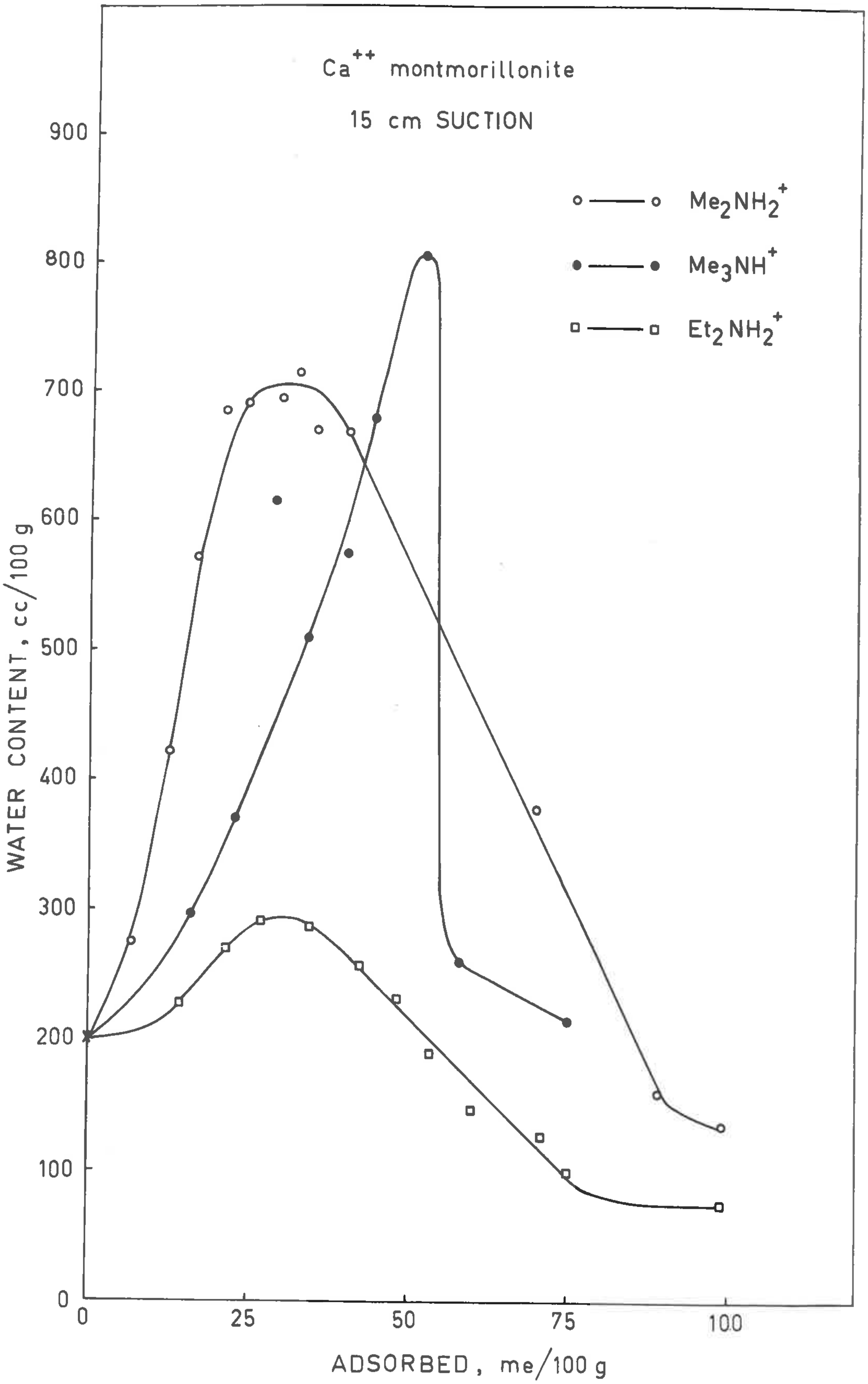
Ca++ montmorillonite
15 cm SUCTION
○ Me1NH3+
● Et1NH3+
△ Pr1NH3+
□ Bu1NH3+
WATER CONTENT, cc/100 g
ADSORBED, me/100 g
0
100
200
300
400
500
600
700
800
900
1000
0
25
50
75
100

Figure 31

Figure 32.

Water content on wetting to pF 1.1 of Ca^{++} montmorillonite cores as a function of the amount of dimethyl-, trimethyl-, and diethylammonium cations adsorbed.



Ca^{++} montmorillonite
15 cm SUCTION
$Me_2NH_2^+$
Me_3NH^+
$Et_2NH_2^+$
WATER CONTENT, cc/100 g
0
100
200
300
400
500
600
700
800
900
ADSORBED, me/100 g
0
25
50
75
100

Figure 32

Figure 33.

Water content on wetting to pF 1.1 of Ca^{++} montmorillonite cores as a function of the amount of triethyl-, tetraethyl-, di-n-butyl-, and tetra-n-butylammonium cations adsorbed.

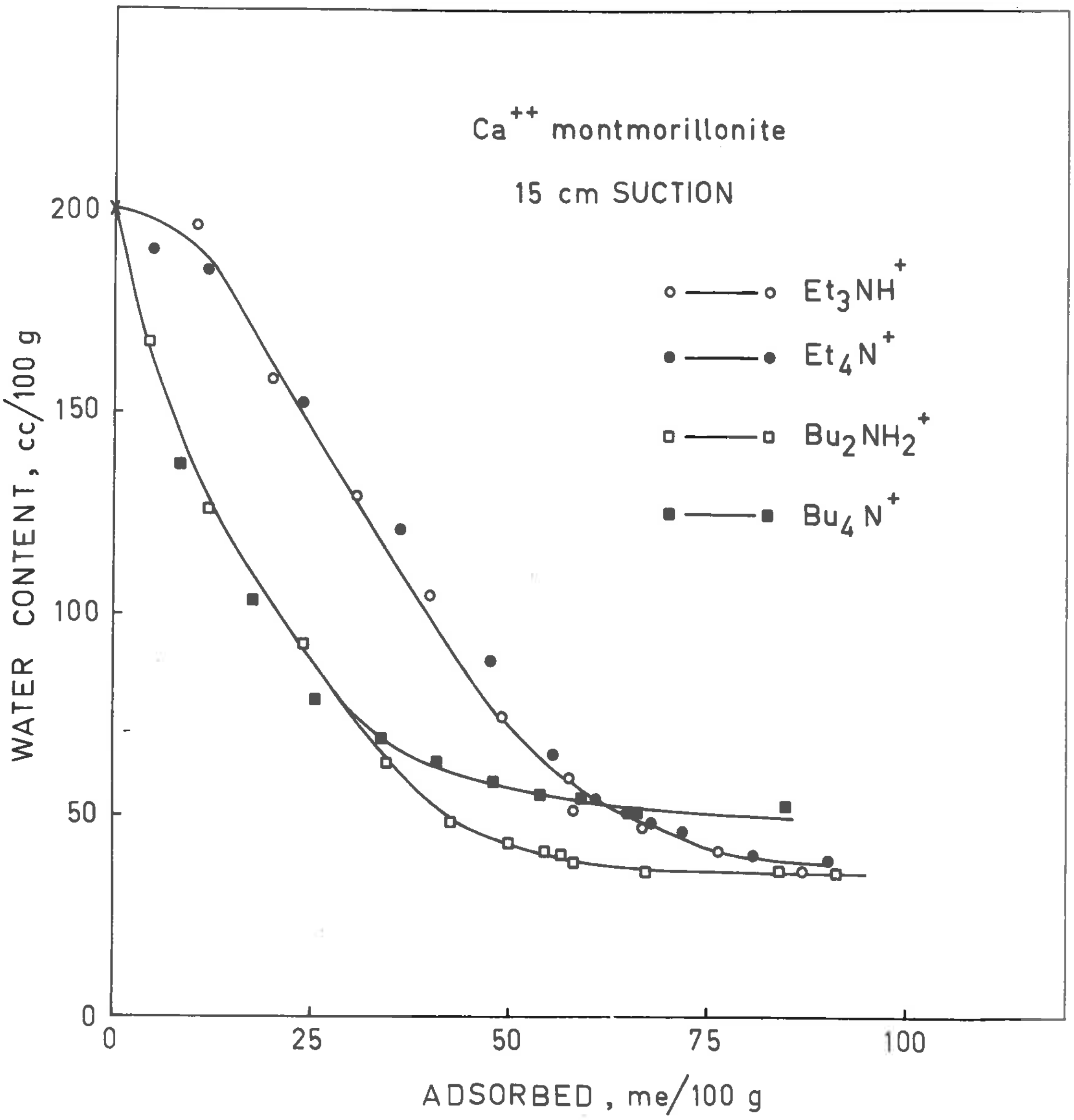

Ca++ montmorillonite
15 cm SUCTION
○——○ Et3NH+
●——● Et4N+
□——□ Bu2NH2+
■——■ Bu4N+
WATER CONTENT, cc/100 g
ADSORBED, me/100 g
0
50
100
150
200
0
25
50
75
100

Figure 33

Figure 34.

Water content on wetting to pF 1.1 of Ca^{++} montmorillonite cores as a function of the amount of sodium, potassium, ammonium, and cesium ions adsorbed.

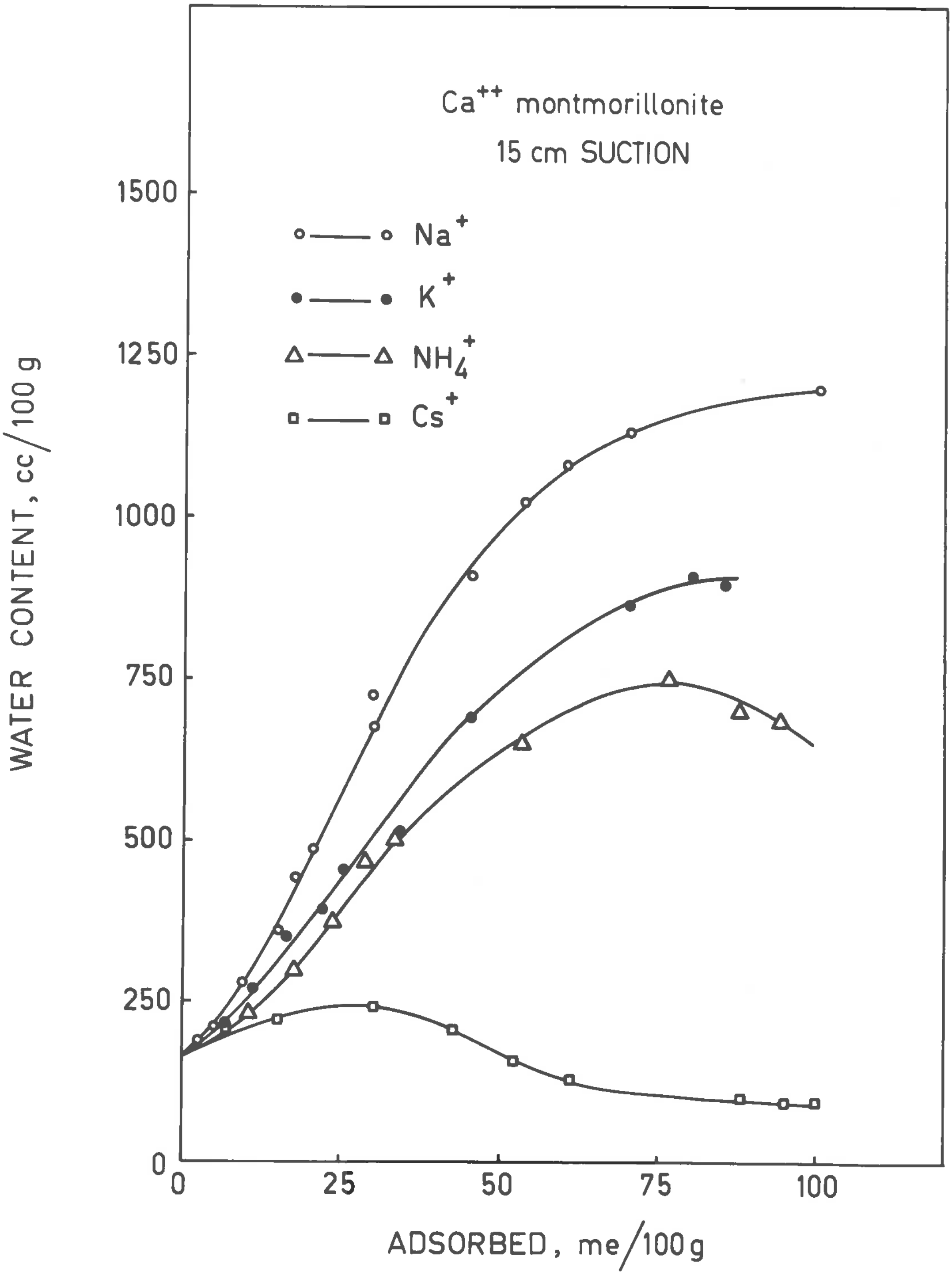

Ca^{++} montmorillonite
15 cm SUCTION
Na$^+$
K$^+$
NH$_4^+$
Cs$^+$
WATER CONTENT, cc/100 g
ADSORBED, me/100 g
0
250
500
750
1000
1250
1500
0
25
50
75
100

Figure 34

Figure 35.

Water vapour sorption isotherms at 20 °C for cores of Ca^{++} montmorillonite and its complexes containing different amounts of monoethylammonium cations.

Relative humidity in per cent.

No.	Amount adsorbed, (me/100 g)
(1)	5.4
(5)	19.5
(9)	38.5
(12)	84.8

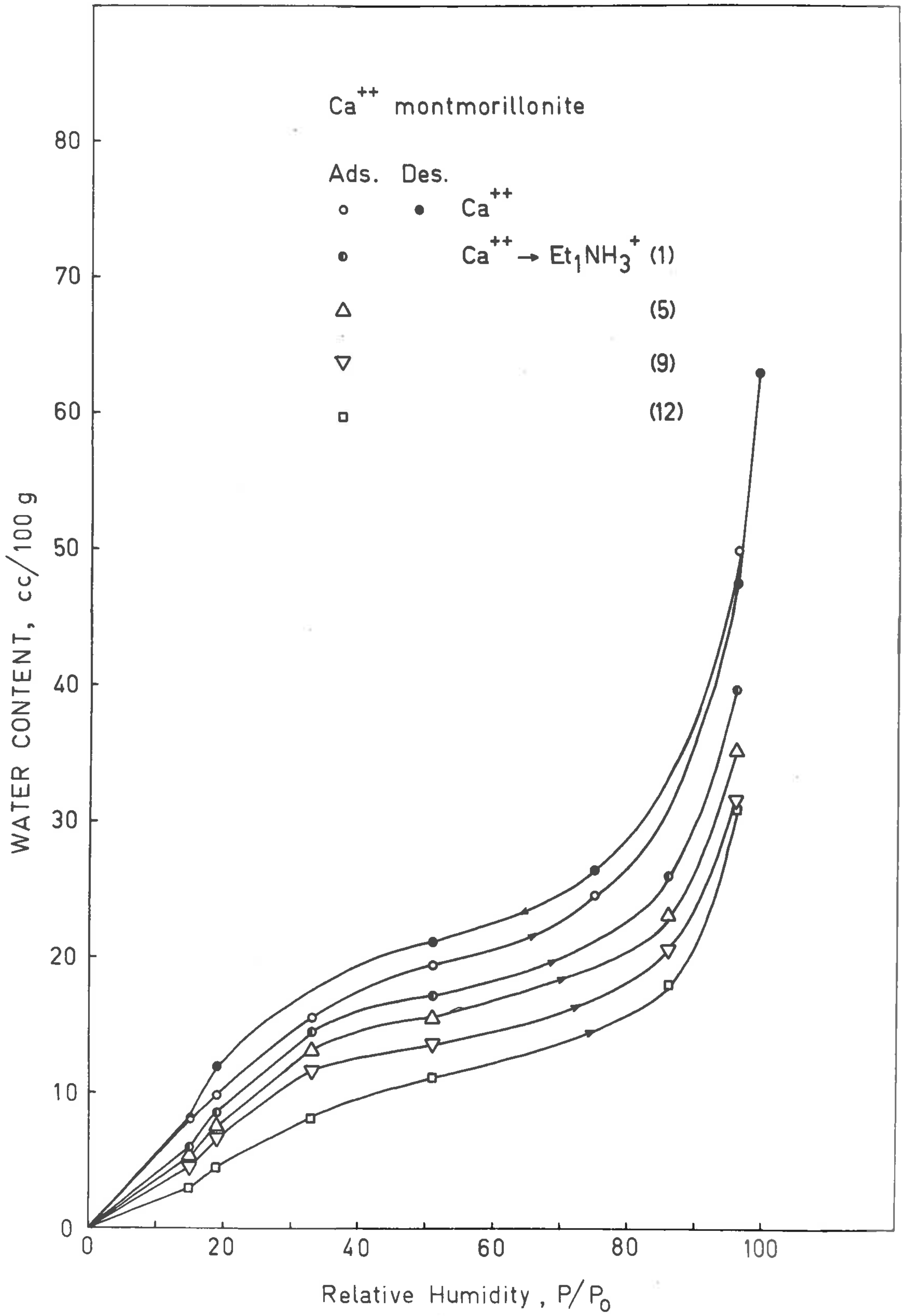

Ca^{++} montmorillonite
Ads. Des.
○ ● Ca^{++}
◐ Ca^{++} → Et$_1$NH$_3^+$ (1)
△ (5)
▽ (9)
□ (12)
WATER CONTENT, cc/100 g
Relative Humidity, P/P$_0$
0
10
20
30
40
50
60
70
80
0
20
40
60
80
100

Figure 35

Figure 36.

Water vapour sorption isotherms at 20 °C for cores of Ca^{++} montmorillonite and its complexes saturated with ethyl-substituted ammonium cations.

Relative humidity in per cent.

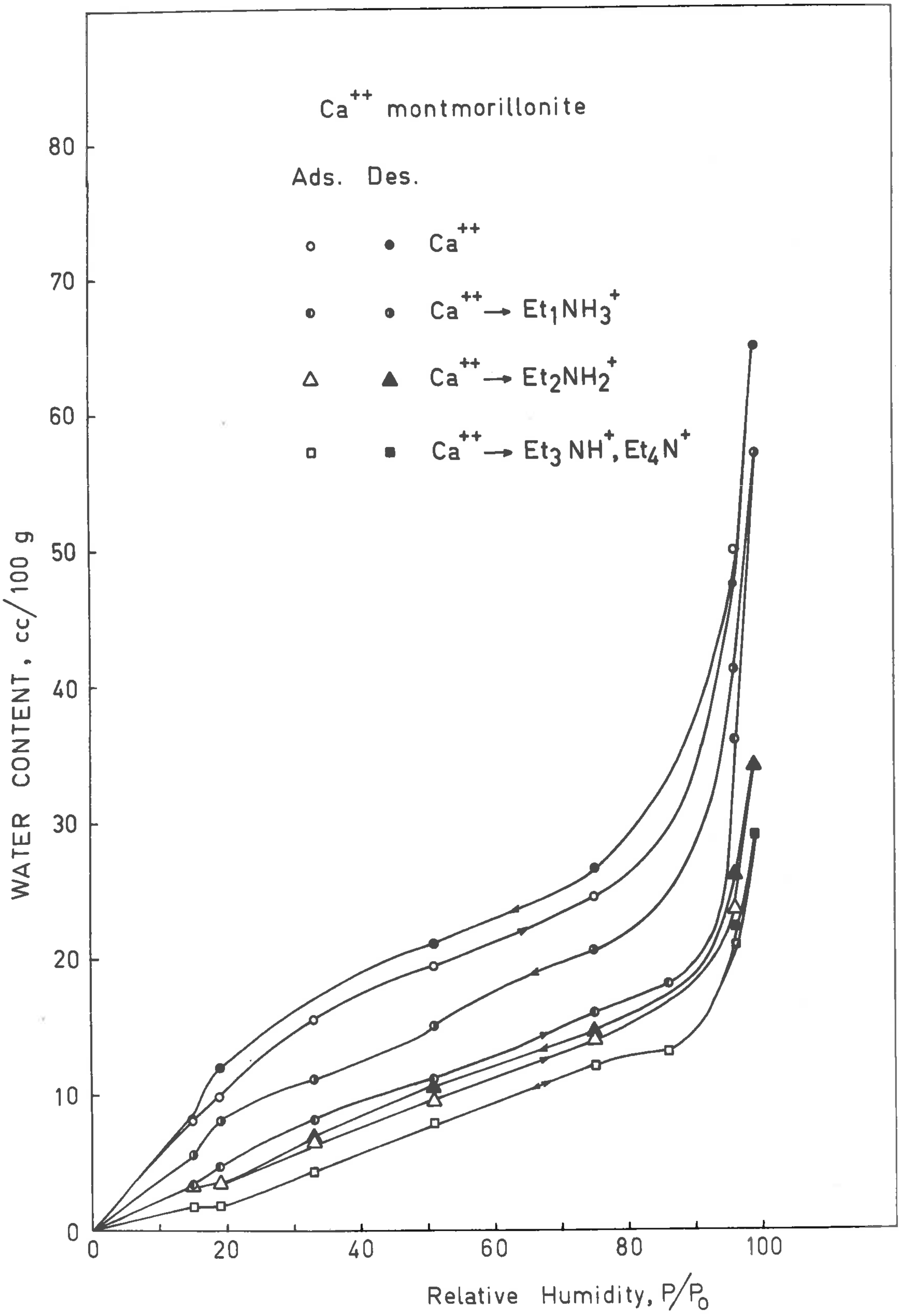

Ca^{++} montmorillonite
Ads. Des.
○ ● Ca^{++}
◐ ◐ Ca^{++} → Et$_1$NH$_3^+$
△ ▲ Ca^{++} → Et$_2$NH$_2^+$
□ ■ Ca^{++} → Et$_3$NH$^+$, Et$_4$N$^+$
WATER CONTENT, cc/100 g
0
10
20
30
40
50
60
70
80
0
20
40
60
80
100
Relative Humidity, P/P$_0$

Figure 36

within a single crystal rather than in a random fashion throughout the crystal. As increasing numbers of layers became saturated with alkylammonium cations the amount of water retained by diffuse double layers was continuously decreased until at complete saturation with the organic cations diffuse double layers were absent and the amount of water held in the interlamellar region will only be a function of the basal spacing and the surface of the clay which was not covered by the organic cations. However, when the water content of complexes saturated with different alkylammonium cations was compared, large variations were observed between individual cations. Complexes with small cations retained larger quantities of water than those saturated with large cations. This indicates that with smaller cations a large proportion of the total water content was probably not associated with clay surfaces but simply enmeshed within the gel structure of the clay-water system (Aylmore and Quirk, 1959, 1960b and c). It is suggested that as diffuse double layers collapsed particle re-arrangement took place. The amount of this re-arrangement will depend on interparticle forces which are determined by the relative adsorption affinities of the alkylammonium cations for the clay surface. It seems probable that with the larger cations which possess greater affinity for the clay surface, less interaction occurs between crystals so that there is only a limited amount of particle re-arrangement. On the other hand, considerable particle re-arrangement occurs in complexes with smaller cations resulting in larger swelling and the creation of an open gel structure in which considerable amounts of water can be retained by surface tension forces.

The complete wetting and drying cycles for complexes saturated with different alkylammonium cations in the range from pF 6.42 to pF 1.1 are shown in Figures 25 to 27. For monoalkylammonium and to a smaller extent for dimethyl- and trimethylammonium complexes the wetting and drying cycles showed a large hysteresis between pF 4.2 and pF 1.1 indicating that a considerable amount of particle re-arrangement had occurred giving rise to an open gel structure. This behaviour contrasts with the virtual absence of appreciable swelling and hysteresis in the wetting and drying cycles of complexes with large cations ($Bu_2NH_2^+$, Et_3NH^+, tetraalkylammonium ions) when presumably the domain structure was preserved (Aylmore and Quirk, 1960a). It is interesting to note that these large cations were adsorbed with a decrease in the standard free energy of 1000 cals/mole or greater and the rate of decrease of swelling with an increase in surface coverage for complexes with these cations was identical (Figure 24). When more than 1/3 of the clay surface was covered the water content of the complexes reached a more or less constant value (40 cc/100 g). This indicates that the presence of diffuse double layers was related to the surface coverage by the organic cations. Evidence for this postulate was provided by studies of negative adsorption of chloride (Schofield, 1947) from a 0.01 N NaCl solution by complexes containing different amounts of tetraalkylammonium cations. At this concentration of NaCl no measurable replacement of adsorbed organic cations by sodium ions occurred. Details of negative adsorption measurements are presented in Appendix VIII. The results were expressed as the volume of solution from which chloride ions were excluded per unit weight of clay and plotted against the surface coverage by the tetraalkylammonium cations (Figure 37). It was observed that a similar relation exists between the volume of exclusion and Θ_r as between swelling and Θ_r (Figure 24). This is further confirmation that diffuse double layers were present for $\Theta_r < 0.3$. The reduction in volume of exclusion with increasing surface coverage appeared at first sight to be due to a reduction in the effective magnitude of the surface density of charge of the clay material by adsorption of the organic cation (Emerson, 1962). This explanation is not valid due to the fact that the repulsion of anions is insensitive to variation in surface density of charge <u>per se</u>. If, however, the adsorption affinity of the organic cation is sufficiently large so that the cation is in physical contact with the clay surface to form a Helmholtz layer and if the cations were adsorbed in discrete layers it is probable that this phenomenon would result in the "inactivation" of areas considerably larger than the area actually covered by the cation. The results indicate that this "critical" area which must be covered by the organic cations to result in "inactivation" was about 1/3 of the total area of the clay.

(ii) <u>Water vapour sorption isotherms</u>.

The water vapour isotherm for Na^+ montmorillonite shows steps each corresponding to a specific threshold pressure (Figures 28 and 29). These steps can be identified with the presence of discrete layers of water molecules in the interlamellar region. (Mooney, Keenan and Wood, 1952<u>b</u>). The phenomenon of step-wise hydration associated with limited

Figure 37.

Volume of exclusion of chloride ions by Na^+ montmorillonite as a function of surface coverage by tetraalkylammonium cations.

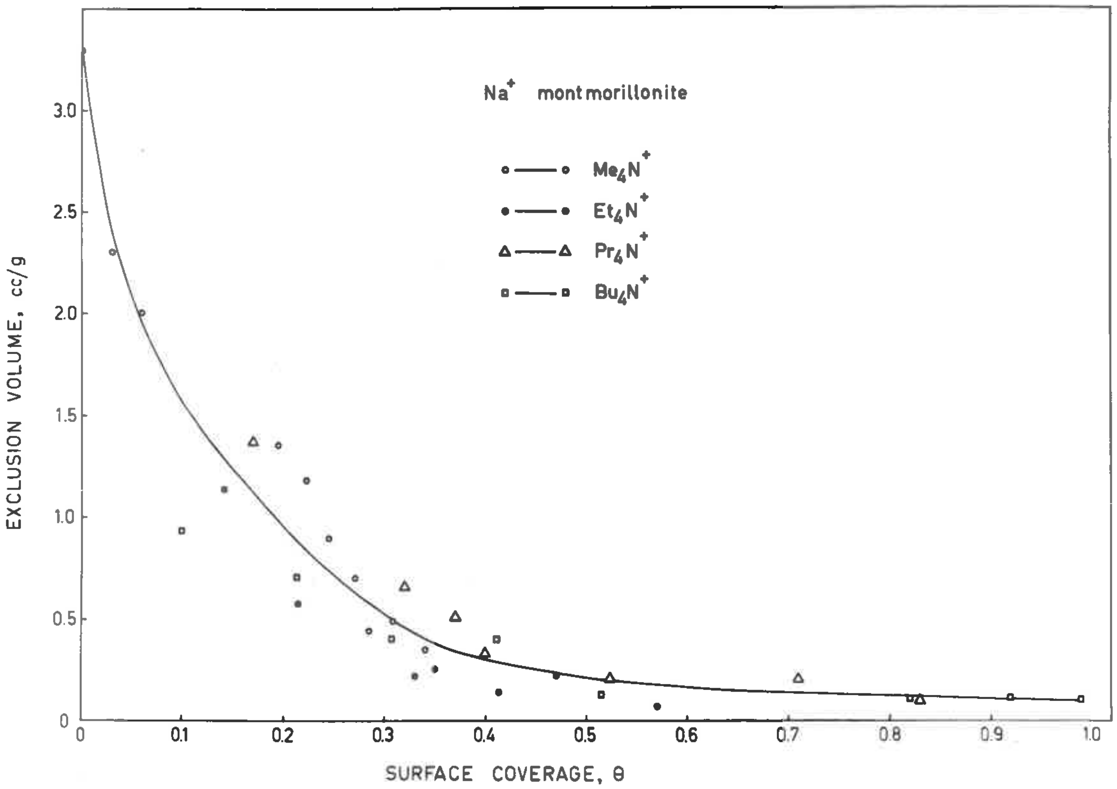

Na$^+$ montmorillonite
Me$_4$N$^+$
Et$_4$N$^+$
Pr$_4$N$^+$
Bu$_4$N$^+$
EXCLUSION VOLUME, cc/g
SURFACE COVERAGE, θ
0
0.5
1.0
1.5
2.0
2.5
3.0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

Figure 37

crystalline swelling of montmorillonite has been observed by many workers (Bradley, Clark and Grim, 1937; Méring, 1946; Norrish, 1954). Complexes partially and fully saturated with monoalkylammonium ions showed similar steps in their isotherms but these steps were less marked than those for Na^+ montmorillonite and decreased in definition as the amount of cations adsorbed increased (Figures 28 and 29). Complexes saturated with larger cations (Et_3NH^+, tetraalkylammonium) did not show similar steps at relative humidity below 0.8 (Figure 30).

The shape of the adsorption isotherm for Na^+ montmorillonite indicated that once the lamellae of the dehydrated clay crystal began to separate after an ill-defined threshold pressure, a monolayer was formed to which successive layers of water molecules were added as the pressure was raised. The absence of a well-defined step below a relative pressure of 0.4 in the isotherms of fully saturated complexes indicated that these complexes were able to take up water vapour without requiring a specific threshold pressure since in this instance the clay lamellae had already been propped apart by the adsorption of the alkylammonium cations in the interlamellar region. The above explanation accounts for the observation that the shape of the isotherms for partially exchanged complexes was intermediate between that of Na^+ montmorillonite and that of the clay fully saturated with alkylammonium, consistent with the postulate that random interstratification of sodium-rich and alkylammonium rich layers within a single crystal occurred.

Figure 28 shows that at low relative humidity the complexes saturated with monoalkylammonium cations adsorbed more water vapour than for the sodium clay whilst at high values of P/P_o the order was reversed. As would be expected the partially saturated complexes sorbed more water vapour at low P/P_o than did Na^+ montmorillonite but less than did the completely saturated complex. At high relative humidity the opposite was observed. These results are consistent with similar observations reported by Barrer and Brummer (1963) for monomethyl- and tetramethylammonium complexes with Na^+ montmorillonite (Figure 29). For complexes saturated with different alkylammonium ions the amount of water vapour sorbed at any given relative pressure decreased as the size of the cation increased. This observation is attributed to the fact that the interlamellar area of complexes with large cations was less than that for those saturated with small cations (see Table 9).

The complete water vapour sorption isotherm for Na^+ montmorillonite and complexes saturated with monoalkylammonium ions exhibited a considerable hysteresis which persisted to the lowest relative humidity (Figure 28). Hysteresis was also present in complexes saturated with the other alkylammonium ions studied but the area enclosed by the adsorption and desorption branches decreased with increasing size of the cation. For larger cations ($Bu_2NH_2^+$, Et_3NH^+, tetraalkylammonium ions) the hysteresis closed at a higher relative pressure than for the smaller cations (Figure 30). Details of the amount of water vapour sorbed at different relative humidity not presented in figures are set out in Appendix IX.

Hysteresis phenomena in water vapour sorption isotherms have frequently been discussed in terms of capillary condensation, ionic hydration and particle re-arrangement. These properties are not readily distinguished quantities but are concomitant and to a certain extent co-operative. The appreciable hysteresis observed for Na^+ montmorillonite is probably due to both particle re-arrangement and ionic hydration since the sodium ion is strongly hydrated. For complexes saturated with alkylammonium ions, ionic hydration was not expected to be an important factor controlling hysteresis since the hydration of alkylammonium cations was relatively less energetic than that of the sodium ions. Comparison between the basal spacings of moist and oven-dry complexes (Table 6) provides further evidence that the adsorbed alkylammonium ions were desolvated on adsorption. It would therefore appear that for complexes saturated with alkylammonium ions most of the hysteresis observed in the water vapour sorption isotherm over the range of P/P_o studied could be attributed to particle re-arrangement. It seems probable that with the bigger alkylammonium cations there was less interaction between crystals so that there is only a limited amount of particle re-arrangement. With the smaller alkylammonium ions there was appreciable hysteresis indicating that considerable particle re-arrangement had occurred. This explanation accounts for the observation that the amount of hysteresis decreased as the size of the organic cations increased.

The area enclosed by the adsorption and desorption branches of the isotherm represents the energy lost per cycle by the clay-water system. In Table 15 the areas of the hysteresis loop for complexes saturated with different alkylammonium ions are summarized.

TABLE 15

Relative areas enclosed by the adsorption and desorption branches of the water vapour sorption isotherm ($P/P_o = 0$ to $P/P_o = 0.99$) for complexes saturated with different alkylammonium cations.

Cation	Relative area	Cation	Relative area
Na^+	100	$Bu_2NH_2^+$	14
$Me_1NH_3^+$	50	Me_3NH^+	22
$Et_1NH_3^+$	55	Et_3NH^+	16
$Pr_1NH_3^+$	48	Me_4N^+	20
$Bu_1NH_3^+$	68	Et_4N^+	14
$Me_2NH_2^+$	43	Pr_4N^+	12
$Et_2NH_2^+$	22	Bu_4N^+	12

The area of the hysteresis loop for Na^+ montmorillonite is assigned a value of 100; the corresponding areas for the alkylammonium complexes prepared from Na^+ montmorillonite are relative to that of the sodium parent clay.

For fully saturated complexes the area covered by the organic cations will determine the amount of water retained by surface adsorption onto the "free" area, that is the area not occupied by alkylammonium ions since the clay lamellae are held permanently apart by the cations. The area covered by the organic cations at saturation was estimated from "Catalin" molecular models as described in chapter III. 3. (see Table 9). The "free" area was simply obtained by difference between the total surface area of the clay and the area covered by alkylammonium ions. The volume of water required to form a single layer over this "free" area (V_m) was then calculated and the relative humidity corresponding to V_m was obtained from the desorption branch of the isotherm. Table 16 summarizes the surface coverage by alkylammonium ions (Θ_r), the "free" area, the calculated monolayer capacity and corresponding relative humidity (P/P_o).

It is interesting to note that for the alkylammonium ions listed in Table 16 the monolayer volume corresponds to a relative humidity of about 0.40 which is the pressure at which the second layer of water molecules was initiated in Na^+ montmorillonite. These calculations provide further evidence for the postulate that alkylammonium ions were adsorbed in a desolvated state and that the amount of water sorbed was only determined by basal spacing and surface area considerations.

IV. 4. 2. Ca^{++} montmorillonite

(i) Water uptake and retention in the range between pF 2.8 and pF 1.1

Figures 31 and 34 show the water content at pF 1.1 of complexes

TABLE 16

Area occupied by alkylammonium ions, "free" area, monolayer coverage by water over "free" area and corresponding relative humidity.

Cation	Amount adsorbed, me/100 g	Area occupied by cations, m^2/g	"Free" area, m^2/g	Monolayer coverage, cc/100g	P/P_o (desorption branch)
$Me_1NH_3^+$	76	111	689	12	0.45
$Et_1NH_3^+$	77	205	595	10.5	0.43
$Pr_1NH_3^+$	77	247	553	9.8	0.41
$Bu_1NH_3^+$	77.5	281	519	9.2	0.38
$Me_2NH_2^+$	89	240	560	9.6	0.38
$Et_2NH_2^+$	87	322	478	8.6	0.47
$Bu_2NH_2^+$	87	567	233	4.6	0.42
Me_3NH^+	84	283	517	9.2	0.40
Me_4N^+	86	295	505	9.2	0.42
Et_4N^+	84	420	380	7.0	0.47

with different alkylammonium cations and monovalent inorganic cations as a function of the amount adsorbed by the clay. The swelling of complexes with monoalkylammonium, dimethylammonium, trimethylammonium, and to a smaller extent with diethylammonium ions showed a maximum when about half of the exchangeable calcium ions originally present on the exchange complex had been replaced by organic cations. No maximum was observed in the swelling of complexes with dibutyl-, triethyl-, and tetraalkylammonium ions. The water content at pF 1.1 for these latter complexes decreased as the amount adsorbed increased. Complexes with monovalent inorganic cations (Na^+, K^+, NH_4^+) showed a continuous increase in swelling as the degree of saturation by these ions increased, except for complexes with cesium ions which behaved similarly to those with large organic cations. Similar relations exist between the water content at pF 2.0 and pF 2.8 and the amount of cations adsorbed (see Appendix VII).

For these reasons, the results will be discussed under three subheadings.

a. Swelling of complexes with monoalkylammonium, dimethylammonium, trimethylammonium, and diethylammonium cations.

Before proceeding to the discussion of the swelling of complexes between Ca^{++} montmorillonite and organic cations, the swelling of the parent calcium clay will be considered.

The water content at pF 1.1 for Ca^{++} montmorillonite was given as 200 cc/100 g of clay which was somewhat greater than the figure quoted by Aylmore and Quirk (1959). However, these workers have subsequently shown that the amount of water retained by Ca^{++} Redhill montmorillonite was dependent on the previous history of the material (Aylmore and Quirk, 1960b). Considerable hysteresis was observed in the wetting and drying cycles between pF 1 and pF 7. This hysteresis was even more marked for material which was prepared from a Na^+ clay suspension and subsequently allowed to dry. The larger value observed in the present work for the water content of Ca^{++} cores (200 cc/100 g at pF 1.1 compared to 91 cc/100 g for the material of Aylmore and Quirk) was attributed to the fact that the material used in the present instance was prepared from a Na^+ clay suspension. It seems probable that this method of preparation gives rise to a more open network which retains a larger amount of water by surface tension forces. The possibility that aluminium impurities were causing the reduction in the water content of the material studied by Aylmore and Quirk was considered. In a preliminary investigation the sodium clay suspension was repeatedly washed with N $CaCl_2$ solution at pH 3 and at pH 7 and the swelling of the two materials was compared. No significant difference in the water content at pF 1.1 was observed between the materials prepared by the two methods. It was therefore concluded that aluminium was not the factor responsible for the difference in water content observed between the present clay material and that used by Aylmore and Quirk.

Since Ca^{++} montmorillonite does not expand beyond a basal spacing of 19 Å, the amount of water retained in the interlamellar region of the crystals only constitutes about 15 per cent of the total water content at pF 1.1. The greater proportion of the water taken up by Ca^{++} montmorillonite must therefore be attributed to intercrystalline swelling and that water which is retained by the gel structure.

The adsorption of alkylammonium ions of class (a) by Ca^{++} montmorillonite below an amount adsorbed of 50 me/100 g resulted in a linear increase in the amount of water taken up by the complexes (Figures 31 and 32). The swelling of the complex containing about 45 me Ca^{++} per 100 g and 45 me monoalkylammonium ions per 100 g was about 2/3 (800 cc/100 g at pF 1.1) of that of Na^{+}montmorillonite (1200 cc/100 g at pF 1.1) and about 4 times that of Ca^{++} montmorillonite (200 cc/100 g at pF 1.1) and 2.5 times that of the clay saturated with monoalkylammonium ions alone.

It is apparent from X-ray analysis of the complexes containing different amounts of monoalkylammonium ions that the increase in the water content below half saturation by the organic ions was due to the formation of diffuse double layers on interlamellar surfaces. It is considered that diffuse double layers were formed in those regions within a single crystal which had both Ca^{++} and monoalkylammonium ions below 60 per cent saturation by the latter. The interaction of diffuse double layers in these regions gave rise to an osmotic repulsive force resulting in adsorption of large quantities of water. Since the clay saturated with monoalkylammonium ion alone showed a basal spacing of 13 Å, when moist, attractive forces between the clay lamellae must become dominant when more than 2/3 of the exchange sites of a given layer within a single crystal had been occupied by the organic cations resulting in the collapse of diffuse double layers and the consequent decrease in swelling. The formation and collapse of diffuse double layers as a function of the amount of organic ions present were accompanied by a decrease and an increase in the mean crystal size, respectively (see Figure 18).

The clay saturated with either calcium alone or monoalkylammonium ions alone did not show extensive crystalline swelling $[d(001) > 30\ \text{Å}]$ whilst a mixture of both ions in equal proportions did. This suggests that the exchange reaction between calcium ions and monoalkylammonium ions at the clay surface involved the release of energy, enabling the system to overcome the potential barrier of limited crystalline swelling $[d(001) < 20\ \text{Å}]$. Such a co-operative effect between two ions which individually only give limited crystalline swelling has not been previously reported and may provide a useful method for studying ionic interaction in aqueous solution. The energy released during the exchange process was thought to be in the form of a net gain in the entropy of the system. Entropy was gained when one of the "bonds" between an interlamellar calcium ion and the clay surface was broken by exchange with a monovalent organic cation. Such a "single-bonded" calcium ion can be regarded as being in a similar energy level to a calcium ion situated on the external crystal surface which has been shown to be involved in diffuse double layer formation (Edwards and Quirk, 1962). Alternatively, the disruption of the ordered structure of the water of co-ordination around the divalent calcium ion (Mathieson and Walker, 1954; Méring, 1946) resulted in a net increase in the entropy of the system. Norrish (1954) has drawn attention to the fact that on the basis of hydration energy, Ca^{++} montmorillonite would be expected to show extensive crystalline swelling. The absence of this was attributed to the larger radius of dielectric saturation of the calcium ion as compared to the sodium ion. The monoalkylammonium ions probably disrupt the water structures and hence decrease the electrostatic attractive forces between the interlamellar cation and the clay surface. This "structure-breaking" property of the alkylammonium ion is attributed to its relatively larger size as compared to the calcium ion and to the fact that the organic cation was probably adsorbed as a desolvated ion (see chapter III. 1. and Table 6 in particular). In view of the above considerations it becomes clear that careful thermodynamic measurements will have to be carried out for a full understanding of the precise mechanism whereby alkylammonium cations modify the crystalline swelling of calcium montmorillonite.

Garrett and Walker (1960) have proposed a different hypothesis to account for the extensive crystalline swelling of vermiculite saturated with monobutylammonium cations. These workers suggested that the organic ions support the water molecules which act as host resulting in the formation of an "ice-berg" structure (Frank and Evans, 1945) or a clathrate compound. This postulate was supported by the observation that the complex with monobutylammonium cations did not swell in water kept at 50°C.

The effect of high temperatures on the swelling of Ca^{++} montmorillonite containing different amounts of monoalkylammonium ions was therefore investigated. For this experiment the cores in equilibrium at pF 1.1 at 20°C were placed on a sintered glass funnel in which water was maintained at a hydrostatic suction of 10 cm. The funnel containing the cores was kept in an electric oven at 70°C for a period of 7-10 days. The water content of the complexes was plotted against the amount of monoalkylammonium ions adsorbed (Figure 38). It was observed that the maximum in the swelling at 20°C for these complexes was absent.

The swelling curves at 70°C showed a steep initial slope followed by a more or less flat plateau when more than half of the exchangeable calcium ions had been replaced by monoalkylammonium ions. The rate of increase in swelling was similar for the monoalkylammonium ions but the plateau swelling was dependent on the size of the cation. The water content at the plateau decreased as the size of the organic ion increased.

These observations are against the hypothesis that the swelling of montmorillonite-monoalkylammonium complexes involved the formation of a clathrate compound between water molecules and organic cations since in the present instance swelling was not inhibited by high temperatures which would be expected to destroy the "ice-berg" structures of Frank and Evans (1945). The absence of a maximum in the swelling at half saturation by monoalkylammonium ions and the dependence of the plateau water content on the size of the organic cation can be explained in terms of the effect of temperature on the relative extent of diffuse double layer formation. According to equation (16) the magnitude of the repulsive potential due to interacting double layers increases with an increase in temperature. It seems probable that once the clay lamellae have been separated, the increase in thermal energy of the interlamellar cations as the temperature was raised was sufficient to overcome the attractive potential between the clay lamellae. The collapse of diffuse double layers when more than 2/3 of the exchange sites had been occupied by the organic ions was therefore prevented. The effect of a rise in temperature on the thermal motion of the adsorbed organic ions was expected

Figure 38.

Water content on wetting to pF 1.0 at 70 °C for Ca^{++} montmorillonite cores as a function of the amount of monoalkylammonium cations adsorbed.

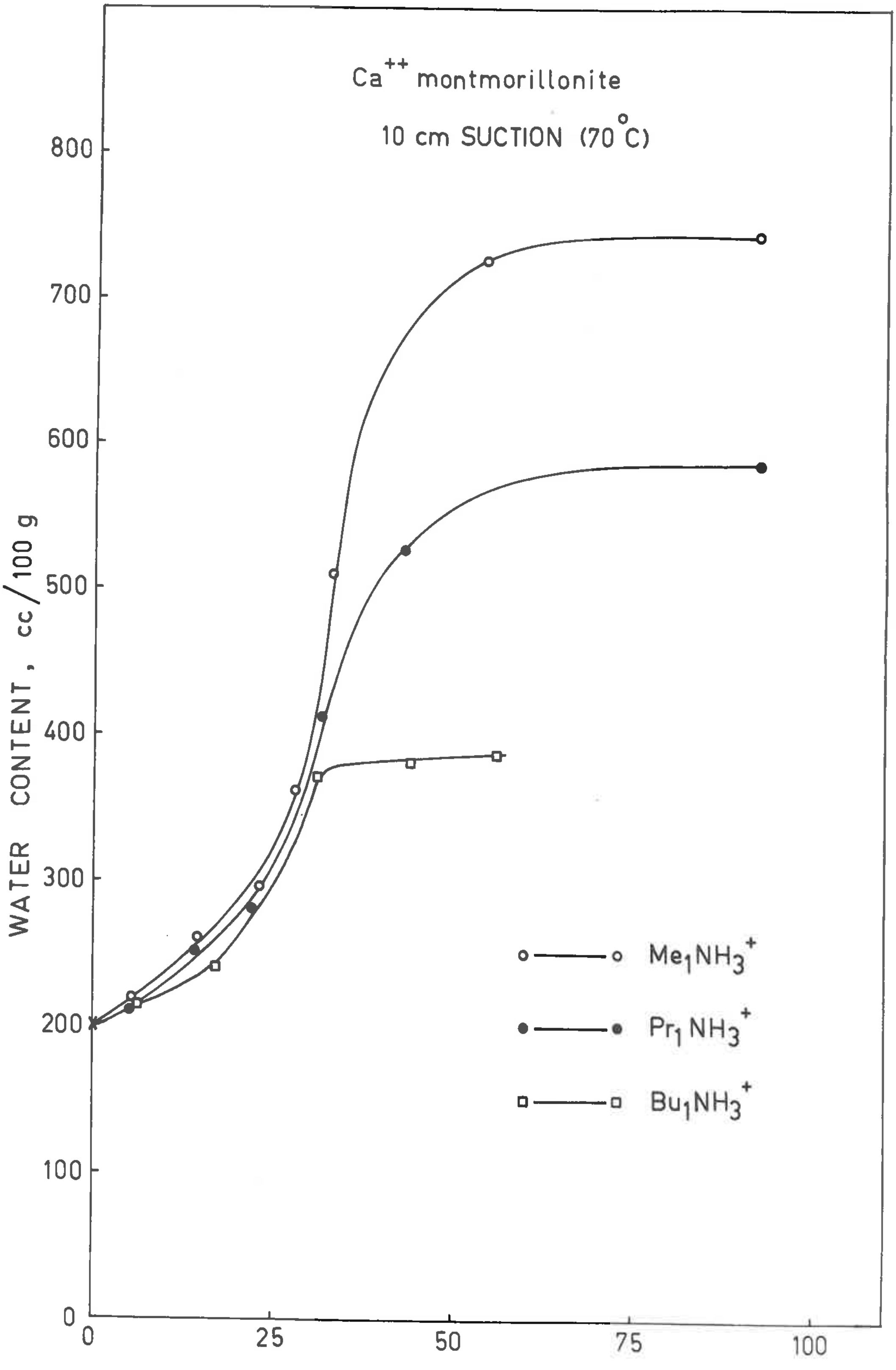

Ca++ montmorillonite
10 cm SUCTION (70 °C)
WATER CONTENT, cc/100 g
ADSORBED, me/100 g
0
100
200
300
400
500
600
700
800
0
25
50
75
100
○——○ $Me_1NH_3^+$
●——● $Pr_1NH_3^+$
□——□ $Bu_1NH_3^+$

Figure 38

to be less for the larger cations and hence the extent of diffuse double layer formation was less for larger cations. This may well explain the observation that the plateau water content decreased as the number of carbon atoms per cation increased.

b. Swelling of complexes with dibutyl-, triethyl-, and tetraalkylammonium cations

In this instance no maximum in swelling was observed for any given amount of organic cations adsorbed (Figure 33). This observation indicates that for any degree of saturation by the organic cations the electrostatic attractive potential between cation and clay surface was greater than the increase in net entropy of the system due to the disruption of the water structures around the calcium ion. The attractive force between organic cation and clay surface is expected to increase with the size of the ion. This increase is attributed to the increase in adsorption affinity and in the hydrophobic property of the cation as the number of hydrocarbon groups per cation increased.

c. Swelling of complexes with monovalent inorganic cations

Complexes with sodium, potassium, and ammonium ions showed a continuous increase in the water content at pF 1.1 as the amount adsorbed increased (Figure 34). Since the clay saturated with monovalent ions alone showed extensive crystalline swelling, much of the increase in water content was due to the formation of diffuse double layers in the interlamellar region of the crystal. Basal spacing measurements of the complexes with Na^+, K^+, and NH_4^+ ions (see Appendix IV) indicate that the exchange of calcium for the monovalent ions occurred in discrete layers within a single crystal similar to that occurring in complexes with alkylammonium ions. Diffuse double layers were presumably formed in those layers which were predominantly saturated with monovalent cations. As exchange progressed the number of such layers increased resulting in a continuous increase in the amount of water retained in these layers by diffuse double layers.

The swelling at pF 1.1 of complexes with cesium ions showed a small maximum when about 30 me of cesium ions per 100 g was adsorbed (Figure 34). It seems probable that the large and virtually unhydrated cesium ion disrupts the water structures around the calcium ion thereby decreasing the electrostatic attraction between cation and clay surface. When more than 35 me of cesium ions per 100 g of clay were present this attraction was probably greater than the increase in net entropy of the system due to the disruption of the water structures resulting in a decrease in swelling.

(ii) Water vapour sorption isotherms

Figure 35 shows that Ca^{++} montmorillonite sorbed considerably more water vapour over the entire range of relative humidity (P/P_o 0. - P/P_o 0.99) than did Na^{+} montmorillonite. The isotherm at 20^{o}C for the calcium clay did not show a change in slope below a relative pressure of 0.32 and both adsorption and desorption branches were of type 2 in Brunauer's classification (1944).

The shape of the isotherm for Ca^{++} montmorillonite can be explained in terms of the hydration properties of the calcium ion.

Mathieson and Walker (1954) have shown that the magnesium ion in Mg^{++} vermiculite is octahedrally co-ordinated with six molecules of water which are arranged in a hexagonal network two molecular layers thick. It is probable that the arrangement of water molecules around the interlamellar calcium ion in montmorillonite is similar to that proposed by Mathieson and Walker (1954) for the magnesium ion in vermiculite. Such an arrangement of the interlamellar water prevents the formation of a single integral layer below a relative humidity of 0.32. Furthermore, it was observed that even after prolonged desiccation over P_2O_5 under vacuum at 20°C the basal spacing of Ca^{++} montmorillonite did not decrease below about 14 Å. This explains the absence of a well-defined threshold pressure at low relative humidity since the clay lamellae were already separated.

The shapes of the isotherms for complexes with alkylammonium ions are similar to that for the parent Ca^{++} montmorillonite clay (Figures 35 and 36). The amount of water vapour sorbed by the complexes decreased as the amount of organic ions present increased indicating that the hydration of alkylammonium ions was less energetic than that of calcium ions. These results are consistent with the postulate that random interstratification of calcium-rich and alkylammonium-rich layers was present within a single crystal.

The adsorption and desorption branches of the isotherm for Ca^{++} montmorillonite showed hysteresis but the area enclosed by the two branches was smaller than that for Na^{+} montmorillonite. It is probable that with calcium ions less interaction occurs between crystals so that there is less particle re-arrangement than with sodium ions.

The hysteresis enclosed by the wetting and drying branches of complexes saturated with different alkylammonium cations was similar to that shown by complexes prepared from Na^+ montmorillonite. The amount of hysteresis decreased as the size of the organic ion increased (Figure 36). The similarity of the isotherms for saturated complexes with small alkylammonium cations (monoalkyl-, dimethyl-, trimethylammonium ions) prepared from calcium and sodium montmorillonite contrasts with the large differences in the water content of pF 1.1 observed between complexes prepared from the two parent clays. These observations can be explained in terms of structural differences between calcium and sodium montmorillonite which did not become apparent until the pF was decreased below 2.0 when the large uptake of liquid water gave rise to considerable particle re-arrangement and hence to differences in the amount of water retained in the gel structure by surface tension forces. For complexes with large alkylammonium ions (dibutyl-, triethyl-, tetraalkylammonium ions) the previous history of the clay material was not important in determining the sorption of water over the entire range of pF from 6.5 to 1.1. These large organic ions are strongly bonded to the clay surface ($-\Delta G^m > 1000$ cals/mole). It is therefore expected that for these large ions particle interaction is less and hence there is only a limited amount of particle re-arrangement.

CHAPTER V.

THE SWELLING OF COMPLEXES BETWEEN MONTMORILLONITE AND POLYVINYL ALCOHOL

V. 1. Introduction

The water-stability of virgin aggregates is due to the presence of organic materials strengthening the pores within the aggregates thus controlling the rate of wetting and preventing incipient failure. Disruption of cultivated aggregates in the field is attributed to rapid uncontrolled wetting and differential swelling (Quirk and Panabokke, 1962). The problem of increasing the water-stability of aggregates is essentially either a problem of controlling the rate of wetting or of restricting swelling.

Of the various synthetic organic polymers found to be effective in promoting aggregation, the uncharged linear flexible polyvinyl alcohol has been shown to be particularly effective in increasing the mechanical strength and water-stability of natural soil aggregates (Emerson, 1956; Williams, 1959). The manner by which polyvinyl alcohol stabilizes soil aggregates is thought to be due to the ability of the molecule to spread over adjacent clay surfaces like a "coat of paint" (Greenland, 1963) or by linking together several clay crystals or domains (Aylmore and Quirk, 1959; Emerson, 1960).

Adsorption of the polymer by the clay appears to be necessary before aggregation takes place. The adsorption of polyvinyl alcohol from aqueous solution onto montmorillonite has therefore been studied in some detail by Greenland (1963). It was concluded that the amount of polymer adsorbed was dependent on the concentration of the clay suspension. The decrease in polymer adsorbed as the suspension concentration increased was attributed to the formation of aggregates around which the polymer was adsorbed.

The purpose of the present work is to relate the swelling of complexes of montmorillonite and polyvinyl alcohol to information obtained from adsorption studies so that the mechanism by which polyvinyl alcohol controls and restricts the swelling of clays might be better understood.

V. 2. Experimental

V. 2. 1. Materials

The polyvinyl alcohols were supplied by the Nippon Synthetic Chemical Corporation, Japan, and have been described previously by Greenland (1963). Two G series samples of molecular weights 80,000 (GH-20) and 25,000 (GL-05) and one N series sample of molecular weight 75,000 (NH-22) have been used.

V. 2. 2. Methods

Complexes of montmorillonite and the polyvinyl alcohols were prepared by adding standard solutions of the polymer to air-dry clay or clay suspension, shaking for 5-7 days, centrifuging the suspension and decanting the supernatant liquid. To examine the effect of clay/polymer solution ratio and the manner in which the polymer solution is mixed with the clay on the swelling of the complexes, the following experiments were carried out:

(i) Solutions of GH-20 and GL-05 were added to air-dry Na^+ montmorillonite to give identical amounts of polymer by weight of clay but having a final suspension concentration of 1, 2, and 4 per cent.

(ii) Solutions of GH-20 and NH-22 were added to Na^+ and Ca^{++} montmorillonite suspensions.

(iii) Solutions of GH-20 were added to air-dry Na^+ and Ca^{++} montmorillonite clay to give a 10 per cent suspension.

The amount of PVA in the supernatant solution, except for the samples prepared by method (iii) was estimated by dichromate oxidation (Greenland, 1963). The centrifuged material was dried in the electric oven at 70 °C and ground to pass a 60 mesh sieve. Cores were manufactured from this material by the method of Aylmore and Quirk (1959, 1960b). The water content at different pF values for complexes containing different amounts of PVA was determined as described in Chapter IV. 2. 2.

V. 3. Results

The water content of cores at pF 1.1 for Na^+ montmorillonite containing different amounts of GH-20, GL-05 and NH-22 is shown in Figures 39 to 41. A similar plot for complexes with Ca^{++} montmorillonite is presented in Figure 42.

Water vapour adsorption isotherms at 20 °C for Na^+ and Ca^{++} montmorillonite with different amounts of GH-20 adsorbed are shown in Figures 43 and 44. From these isotherms the difference in swelling pressure between the complexes with different amounts of PVA adsorbed and the parent clay material was calculated from the relationship (Helfferich, 1962, p. 111)

$$RT \ln \frac{P_w}{P'_w} = (\pi - \pi') v_w \qquad \ldots\ldots(42)$$

where P_w and P'_w are the partial pressures of the complex and the parent clay, respectively; R is the gas constant and T is the absolute

Figure 39.

Water content on wetting to pF 1.1. of Na^+ montmorillonite cores containing different amounts of polyvinyl alcohol (GH-20).

■——■	Polymer solution added to clay suspension.
□——□	Polymer solution added to air-dry clay to give a final suspension of 10 per cent.
○——○	Polymer solution added to air-dry clay to give a final suspension of 1 per cent.
●——●	Polymer solution added to air-dry clay to give a final suspension of 2 per cent.
△——△	Polymer solution added to air-dry clay to give a final suspension of 4 per cent.

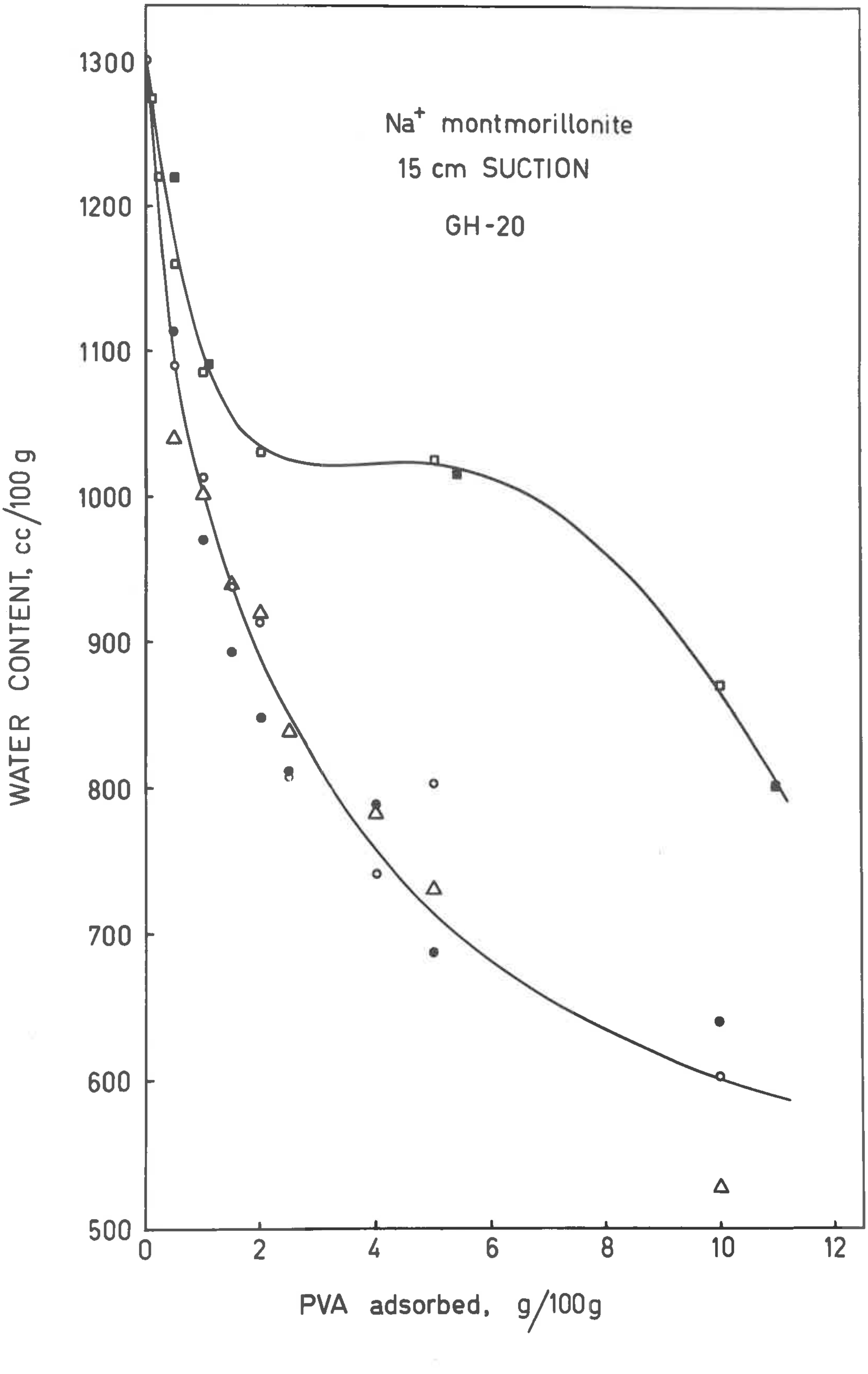

Na$^+$ montmorillonite
15 cm SUCTION
GH-20
WATER CONTENT, cc/100 g
1300
1200
1100
1000
900
800
700
600
500
0
2
4
6
8
10
12
PVA adsorbed, g/100g

Figure 39

Figure 40.

Water content on wetting to pF 1.1 of Na^+ montmorillonite cores containing different amounts of polyvinyl alcohol (GL-05).

○ ——— ○	Polymer solution added to air-dry clay to give a final suspension of 1 per cent.
● ——— ●	Polymer solution added to air-dry clay to give a final suspension of 2 per cent.
△ ——— △	Polymer solution added to air-dry clay to give a final suspension of 4 per cent.

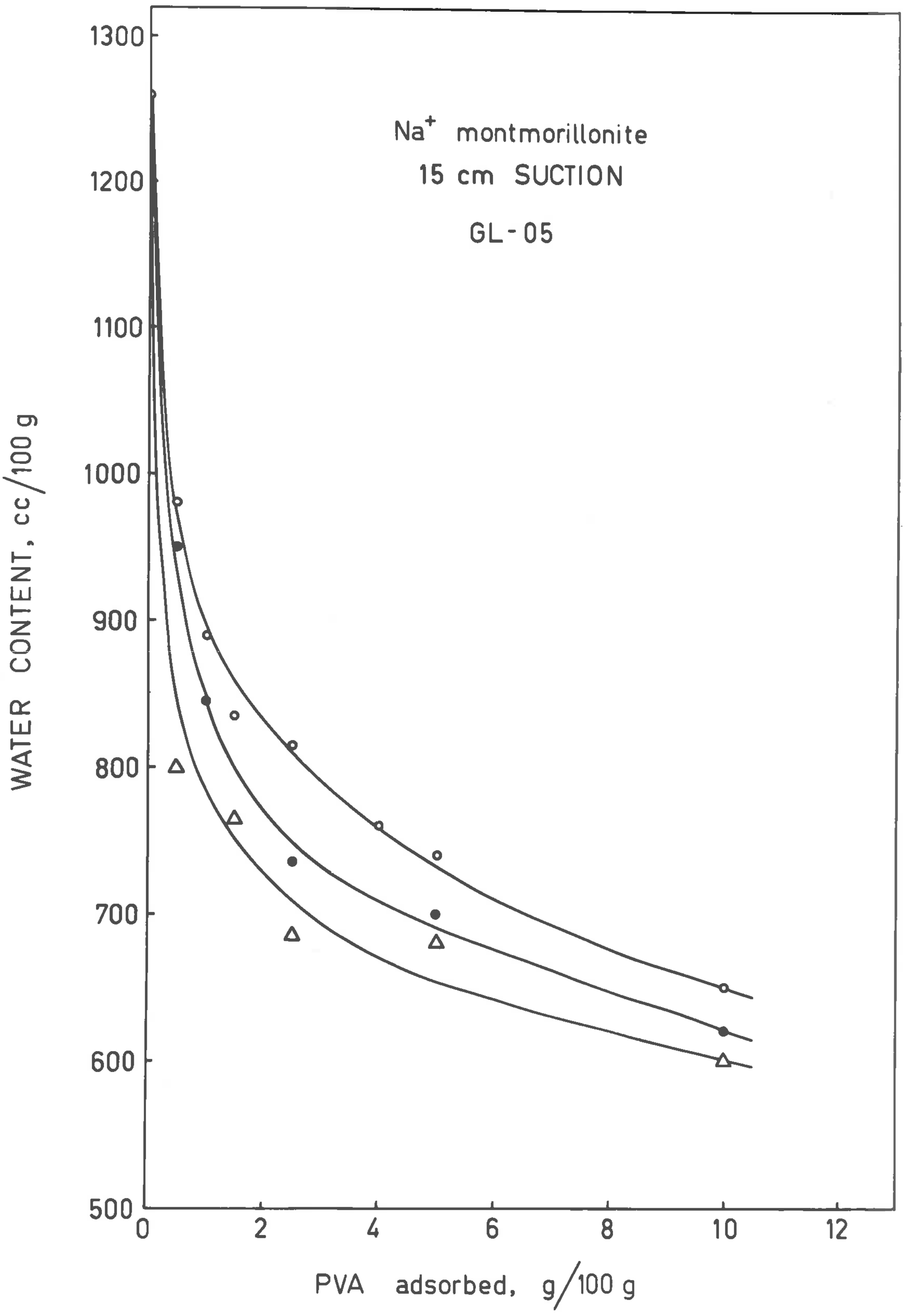

Na$^+$ montmorillonite
15 cm SUCTION
GL-05
WATER CONTENT, cc/100 g
1300
1200
1100
1000
900
800
700
600
500
0
2
4
6
8
10
12
PVA adsorbed, g/100 g

Figure 40

Figure 41.

Comparison between two polyvinyl alcohols in controlling the swelling of montmorillonite. Water content on wetting to pF 1.1 of Na^+ montmorillonite cores containing different amounts of polyvinyl alcohol (GH-20 and NH-22).

Polymer solution added to an approximately 1 per cent clay suspension.

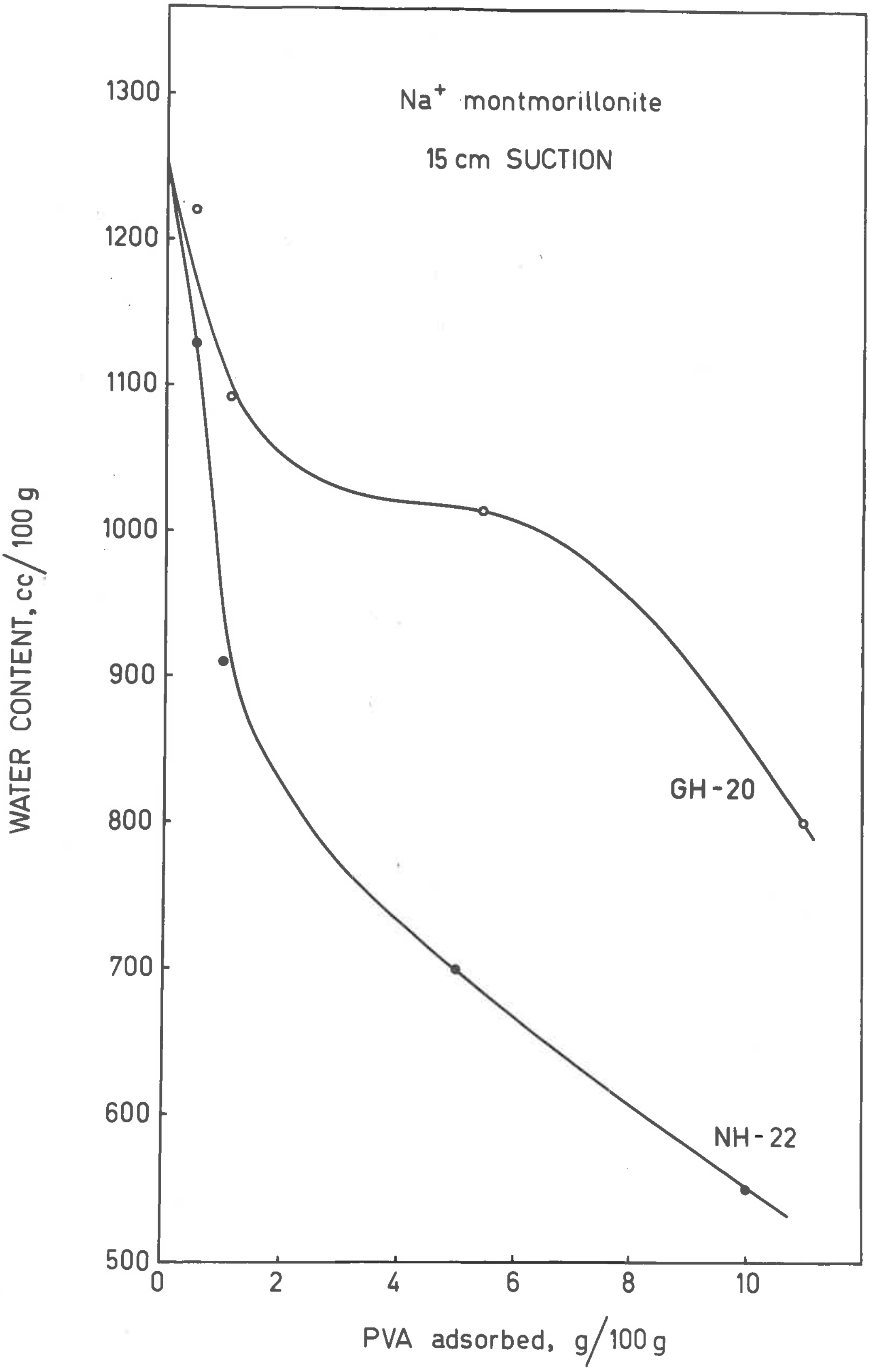

Na$^+$ montmorillonite
15 cm SUCTION
WATER CONTENT, cc/100 g
1300
1200
1100
1000
900
800
700
600
500
0
2
4
6
8
10
GH-20
NH-22
PVA adsorbed, g/100 g

Figure 41

Figure 42.

Water content on wetting to pF 1.1. of Ca^{++} montmorillonite cores containing different amounts of polyvinyl alcohol.

△——△	GH-20.	Polymer solution added to air-dry clay to give a final suspension of 10 per cent.
○——○	GH-20.	Polymer solution added to clay suspension.
●——●	NH-22.	Polymer solution added to clay suspension.

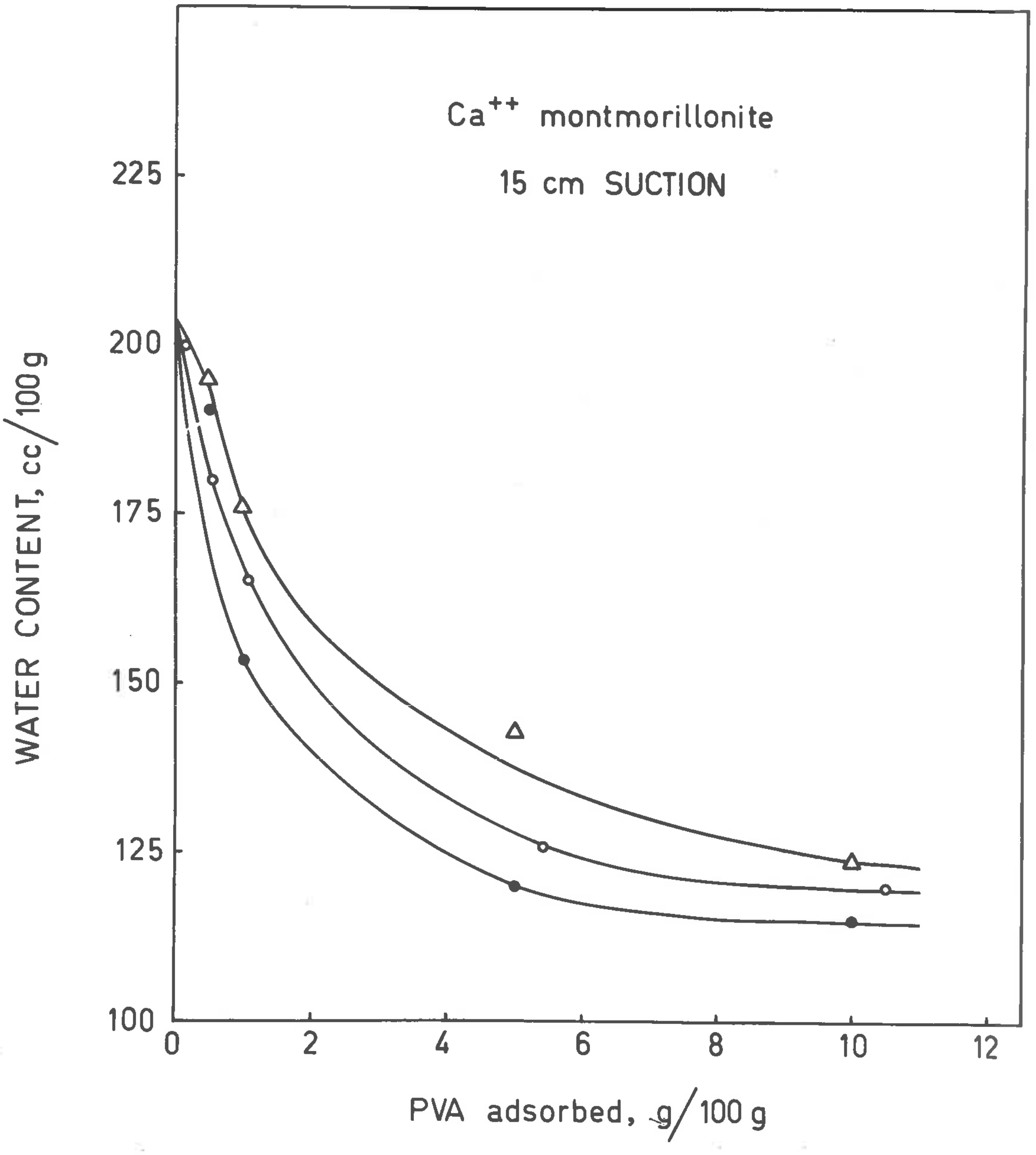

Ca^{++} montmorillonite
15 cm SUCTION
WATER CONTENT, cc/100 g
225
200
175
150
125
100
0
2
4
6
8
10
12
PVA adsorbed, g/100 g

Figure 42

Figure 43.

Water vapour sorption isotherms at 20 °C for Na^+ montmorillonite with different amounts of polyvinyl alcohol (GH-20) adsorbed. Relative humidity in per cent.

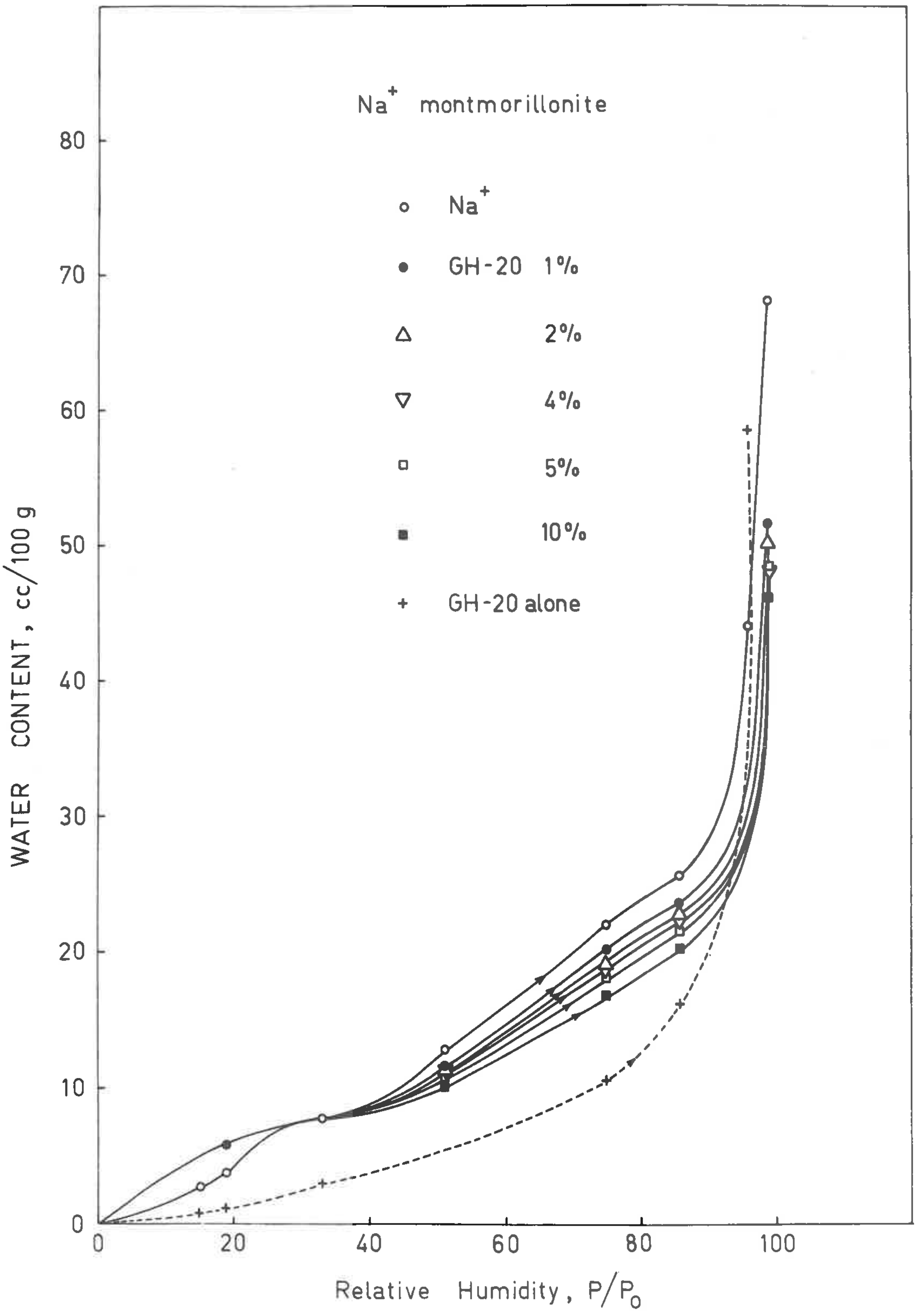

Na$^+$ montmorillonite
○ Na$^+$
● GH-20 1%
△ 2%
▽ 4%
□ 5%
■ 10%
+ GH-20 alone
WATER CONTENT, cc/100 g
Relative Humidity, P/P$_0$
0
10
20
30
40
50
60
70
80
0
20
40
60
80
100

Figure 43

Figure 44.

Water vapour adsorption isotherms at 20 °C for Ca^{++} montmorillonite with different amounts of polyvinyl alcohol (GH-20) adsorbed. Relative humidity in per cent.

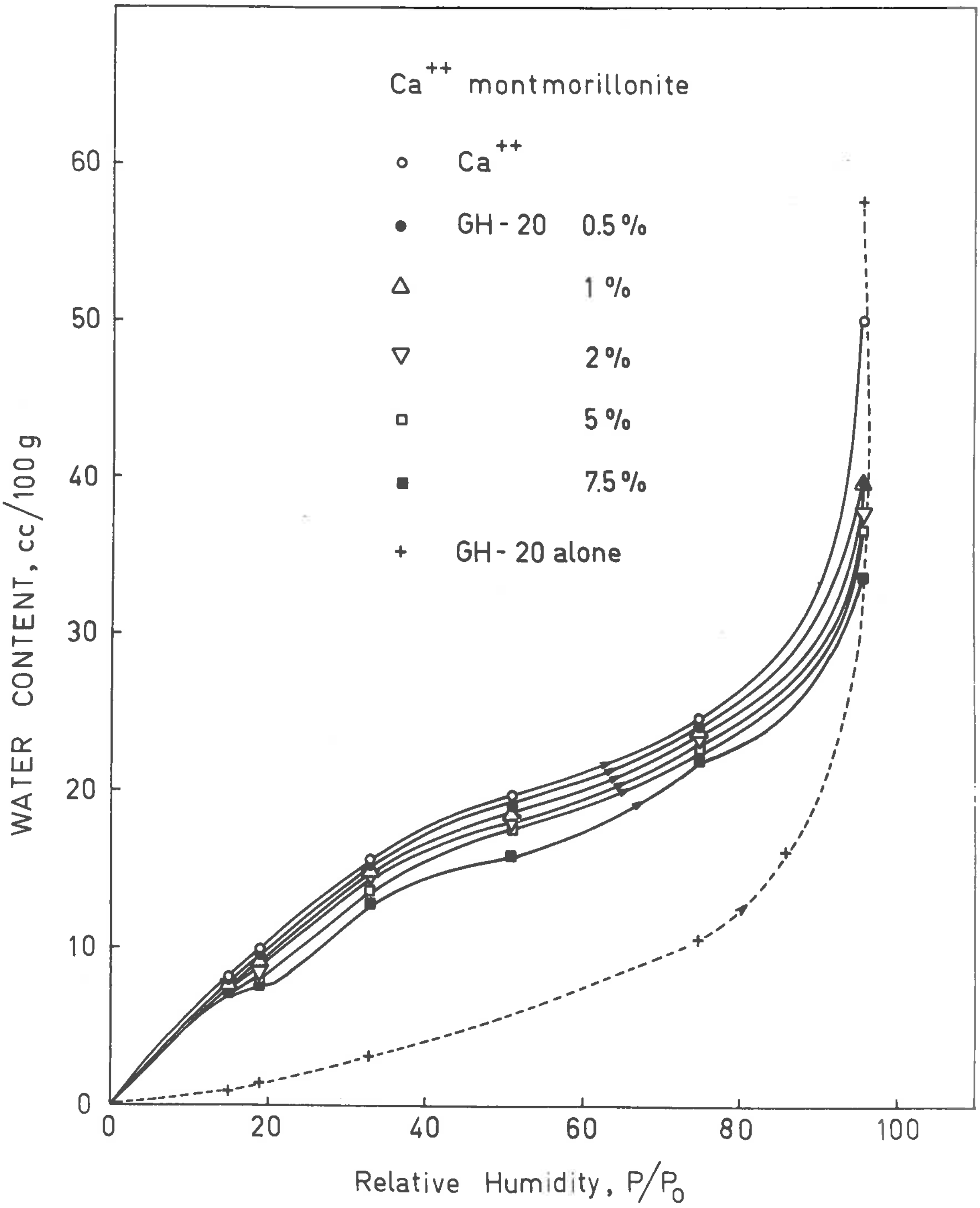

Ca^{++} montmorillonite
○ Ca^{++}
● GH - 20 0.5 %
△ 1 %
▽ 2 %
□ 5 %
■ 7.5 %
+ GH - 20 alone
WATER CONTENT, cc/100 g
Relative Humidity, P/P$_0$
0
10
20
30
40
50
60
0
20
40
60
80
100

Figure 44

Figure 45.

Difference in swelling pressure between montmorillonite-polyvinyl alcohol complexes and the parent clay material as a function of the amount of polyvinyl alcohol (GH-20) adsorbed.

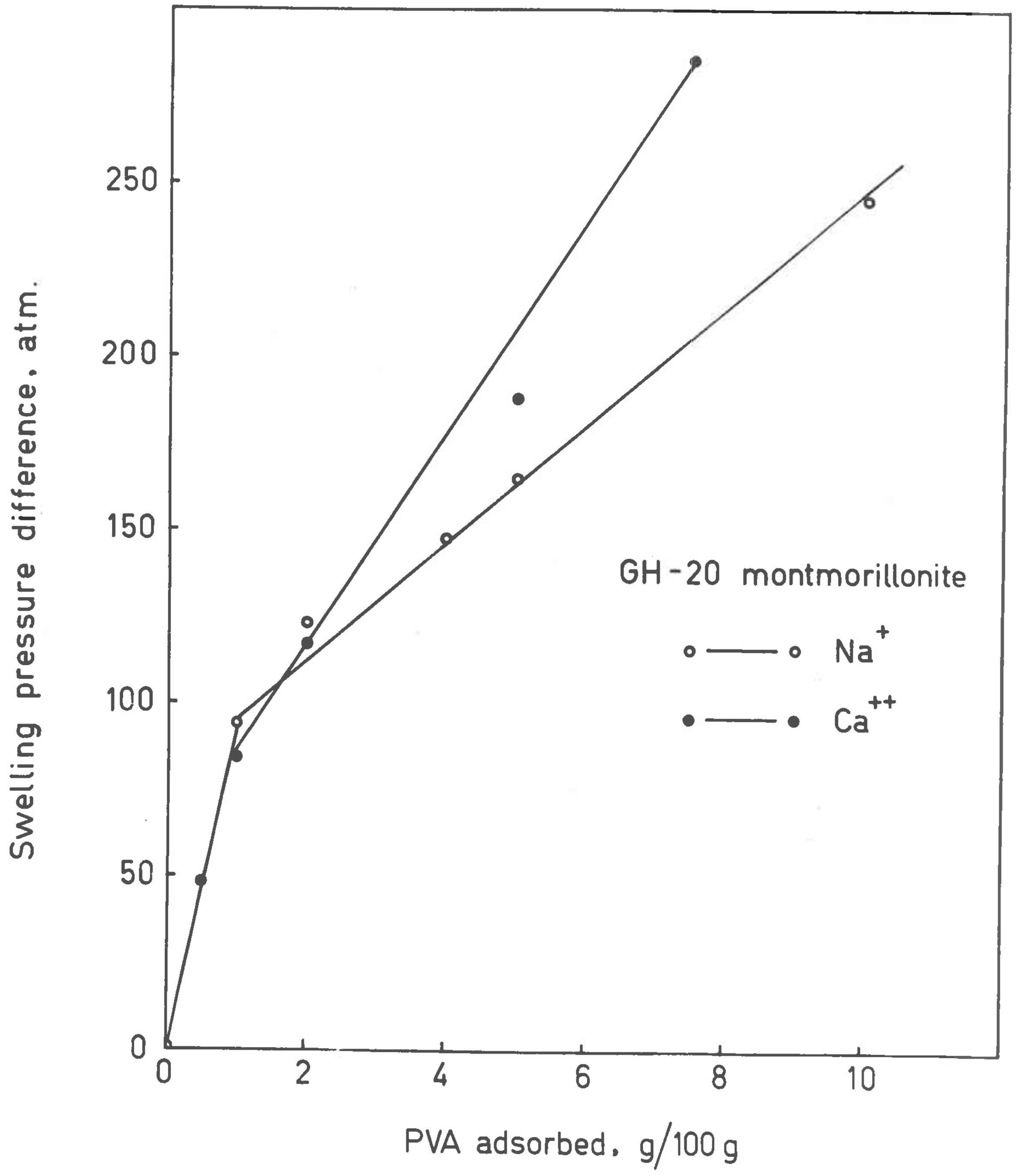

Swelling pressure difference, atm.
0
50
100
150
200
250
0
2
4
6
8
10
PVA adsorbed, g/100 g
GH-20 montmorillonite
○——○ Na⁺
●——● Ca⁺⁺

Figure 45

temperature. π and π' refer to the swelling pressure of the complex and the parent clay, respectively; v_w is the molar volume of water. Swelling pressures were calculated at a water content of 20 cc/100 g of oven-dry clay and the results are plotted in Figure 45.

V. 4. Discussion.

(i) Ca^{++} montmorillonite

Since Ca^{++} montmorillonite does not expand beyond a basal spacing of 19 Å, only a small part of the total water content at pF 1.1 was present in the interlamellar region (30 cc/100 g). The greatest part of the water adsorbed was associated with the external crystal surfaces and contained in the pore structure of the clay mass (gel or structural water). The amount of water enmeshed within the gel structure is dependent on the previous history of the clay. It has been shown that Ca^{++} montmorillonite cores prepared from a Na^{+} clay suspension adsorbed considerably more water at pF 1 than cores which were obtained by simply replacing the cations present in the original material by washing with $CaCl_2$ solution (Aylmore and Quirk, 1960b). The more open structure of complexes prepared by adding PVA solution to the clay suspension as compared to those formed by mixing the polymer solution with air-dry clay, may well explain the larger swelling of the former (Figure 42). The figure also shows that the swelling of NH-22 complexes was less than the corresponding GH-20 complexes. The greater effectiveness of the NH-22 polymer in reducing the water uptake may be due to the larger average particle size of the polymer which is known to form intramolecular hydrogen bonds. In solution, NH-22 forms a rather viscous gel (Greenland, 1963) in which the clay particles appeared to be embedded when seen under phase contrast. Such a network of clay and polymer may form a very rigid structure on oven-drying and this would resist a large increase in volume (swelling) when water was adsorbed. It is also possible that aggregates of the polymer blocked the pores within the clay mass (Williams, 1959) thus reducing the amount of gel water.

The reduction in the swelling of complexes is attributed to interparticle bonding of several clay particles or domains by the polymer probably through hydrogen bonding between the hydroxyl groups of the polymer and the oxygen atoms of the clay surface (Emerson, 1956; Greenland, 1963). If a two-dimensional surface configuration of the polymer molecule is assumed and no interlamellar penetration occurred, the amount of polymer required to form a layer of 10 Å thick over the external crystal area (120 m^2/g) is about 12 g/100 g of clay. The results show that no further reduction in swelling occurred beyond an amount adsorbed of 6 g of polymer per 100 g of clay. However, if bridging between domains rather than between individual clay crystals took place, a much smaller amount of polymer would be required to effect a large reduction in swelling since the external domain area would be considerably less than the external crystal area. The small hysteresis in the pF-water content relationship of Ca^{++} montmorillonite provides further evidence of the existence of a high degree of oriented stacking of the crystals into domains.

The water vapour adsorption isotherm (Figure 43) shows that at low values of relative humidity ($P/P_o < 0.4$) water uptake by complexes with Na^+ montmorillonite was more or less independent of the amount of polyvinyl alcohol adsorbed. At low relative humidity the water molecules adsorbed are those resulting from the hydration energy of the exchangeable cations. At higher relative humidity the uptake of water is accompanied by swelling and is therefore dependent on the degree of interparticle bonding. This explanation accounts for the observation that the amount of water adsorbed was least for complexes containing the largest amount of polymer adsorbed.

For complexes with Ca^{++} montmorillonite (Figure 44) differences in the amount of water adsorbed as a function of the amount of polyvinyl alcohol present, persist to the lowest relative humidity. This observation is attributed to the fact that in this instance the clay lamellae in a crystal were already separated (see IV. 4. 2.).

The dependence of the amount of water adsorbed on the quantity of polymer present is similar to that shown by synthetic ion-exchange resins. It has been shown that the swelling of cross-linked ion-exchange resins is reduced as the degree of cross-linking is increased (Boyd and Soldano, 1953). This reduction is attributed to the increase in rigidity of the system as the number of cross-links increases. Figure 45 shows that the swelling pressure of the clay-polymer complexes increases as the amount of polymer present is increased. This is considered as evidence that the mechanism whereby polyvinyl alcohol restricts the swelling of clays is through interparticle (interdomain) linking. It is interesting to note that the greatest increase in swelling pressure was observed below 1 per cent of polymer present. It would appear that the first few cross-links established between domains were the most effective in restricting volume increase. Further additional links contribute relatively less towards stabilizing the structure and this would explain the initial steep fall followed by a levelling off in the rate of swelling with increasing amounts of polyvinyl alcohol adsorbed.

(ii) Na^+ montmorillonite

Figure 39 shows the water content of pF 1.1 for complexes with GH-20 as a function of the amount of polymer adsorbed. For complexes prepared by adding polymer solution to air-dry clay powder to give final suspension concentrations of 1, 2, and 4 per cent, the decrease in swelling as the amount of polymer present increased was more or less identical. When either the suspension concentration was increased to 10 per cent or where the polymer solution was mixed with the clay suspension (final suspension concentration 2.4 per cent) the resulting complexes adsorbed considerably larger amounts of water for any given quantity of polymer present. Complexes with GL-05 prepared by mixing polymer solution with air-dry clay showed differences in swelling depending on the ratio of clay to polymer solution. Complexes formed from a 4 per cent suspension concentration showed the least swelling whilst those prepared from a 1 per cent concentration adsorbed the largest amount of water (Figure 40).

These observations can be explained in terms of the surface area available for adsorption, the mean distance of separation between clay particles, and the length of the polymer molecule. In a dilute aqueous suspension of Na^+ montmorillonite interlamellar separations

> 100 Å have been reported (Norrish, 1954). The surface area under these conditions measured from chloride repulsion studies is in the order of 560 m^2/g, compared to 85 m^2/g for the external crystal area of Ca^{++} montmorillonite (Edwards and Quirk, 1963). A large area would favour adsorption by providing sites for attachment of the polymer molecule, whilst large interparticle distances would reduce the probability of interparticle bonding. Other things being equal, the higher molecular weight polymer (GH-20) because of its length will be more effective in forming cross-links than will GL-05 which is shorter.

If swelling is inversely related to the degree of cross-linking a decrease in suspension concentration is expected to reduce the frequency of interparticle bonding. The results for GH-20 (Figure 39) indicate that this frequency was not reduced by decreasing the suspension concentration from 4 to 1 per cent. It would appear that in this instance the polymer was of sufficient length to form interparticle bridges. On the other hand, the frequency of cross-links was reduced in the case of GL-05 when the concentration of the suspension was decreased and consequently, the swelling of the complexes prepared from a 1 per cent suspension was greater than that of the cores prepared from a 4 per cent suspension. This indicates that the length of the polymer molecule capable of forming cross-links between clay particles was the factor which controls the frequency of interparticle bonding.

Suspension concentration is not the only factor responsible for determining the amount of water taken up by the complex. The larger water contents obtained for complexes formed by adding polymer solution to clay suspension was attributed to the larger amount of water enmeshed within the gel structure. For the same final suspension strength complexes prepared by adding polymer solution to an already flocculated clay system swelled much less than those formed by mixing solution with a dispersed clay system. In the flocculated system, the polymer molecule may spread over adjacent clay surfaces like a "coat of paint" (Greenland, 1963) which would stabilize further the condensed structure and thus reduce swelling. If the above interpretation is correct, the complexes prepared by adding polymer solution to air-dry clay to give a 10 per cent suspension is expected to take up the least amount of water since in this instance both interparticle bonding and "coat of paint" mechanisms would be favoured. The results, however, are contrary to expectation. At this suspension concentration it was impossible to attain uniform mixing conditions. It was observed that on adding the polymer solution to the clay powder the solution did not penetrate to the bottom layers of the clay in the tube even after standing for 4 hours. The upper layers of the clay swelled blocking downward diffusion of the polymer. On stirring with a glass rod, the system became a thick paste. Once the polymer had been adsorbed by the clay particles which first came in contact with the polymer solution, the polymer molecule was "inactivated" since the adsorption process was practically irreversible (Greenland, 1963). Only a fraction of the clay material was involved in adsorption of the polymer and this would explain the larger swelling observed in this instance.

NH-22 was found to be more effective in restricting swelling than GH-20 under the same conditions of mixing and clay to solution ratio

(Figure 41). The explanation is the same as that which has been put forward for the corresponding complexes with Ca^{++} montmorillonite.

The dependence of the swelling pressure on the amount of polymer adsorbed (Figure 45) may be interpreted in the same manner as for the corresponding complexes with Ca^{++} montmorillonite.

It is concluded that the manner in which polyvinyl alcohol controls the swelling of montmorillonite is chiefly by interparticle bonding. The degree and frequency of interparticle bonding is dependent on the initial concentration of the suspension, the mean length of the polymer molecule and the mean interparticle distance. The previous history of the clay system is also important in determining the amount of swelling. When the polymer solution is added to an already aggregated system, a "coat of paint" mechanism may stabilize further the condensed structure by strengthening the pores within the aggregate. This mechanism may be important in controlling the rate of wetting rather than restricting swelling (Williams, 1959).

CHAPTER VI

GENERAL DISCUSSION

The aim of the present work was to study the effect of adsorbed organic compounds on the hydration and swelling of clays. For this reason the processes by which organic compounds were adsorbed by clay minerals will first be considered before proceeding to a discussion of the mechanism whereby organic compounds modify and control clay swelling.

In the present instance the adsorption of homologous series of alkyl-substituted ammonium compounds by montmorillonite was studied. It was shown that adsorption occurred by a cation exchange mechanism and the process was dependent on the number of exchange sites on the clay surface and on the molecular properties of the adsorbate.

The adsorption of alkylammonium ions from an aqueous solution onto sodium montmorillonite could satisfactorily be described in terms of a simultaneous competition (Langmuir, 1916) between the organic ion and the sodium ion for the exchange sites on the clay surface provided that interaction between adsorbed molecules was negligibly small and adsorption sites were uniform. When the size of the organic cation was of the order of magnitude of the area per exchange site significant interaction between adsorbed molecules occurred and hence the "Langmuir" treatment was not valid.

Alternatively, the adsorption of alkylammonium cations may be considered as a heterogeneous ion-exchange equilibrium between the organic ion in solution and the sodium ion in the clay phase. This treatment is identical with the classical mass-action treatment and was satisfactory when applied to the adsorption of small organic cations. With larger cations, however, deviations from theory were observed. These deviations were attributed to molecular interaction at the clay surface and to the "cover-up" effect (Hendricks, 1941).

Within each homologous series the free energy of adsorption increased in a linear fashion with the molecular weight of the adsorbate. However, the increment in - ΔG^m per - CH_3 group was greatest for methyl- and least for butyl-substituted ammonium compounds. These observations have been attributed to the size and the shape of the adsorbate molecule and to the influence of alkyl groups on the basicity of the alkylammonium compounds. Within a given homologous series, the contribution of van der Waals forces to the free energy of adsorption increased with the molecular weight of the adsorbate. The shape factor was reflected by the fact that those cations which permit more intimate contact with the clay surface were more strongly adsorbed than irregularly shaped cations of comparable molecular weight. It has been suggested that the addition of an alkyl group to the central nitrogen atom has a greater effect on the basicity of the cation than when addition occurred to a side chain carbon atom since the inductive (+I) effect falls off rapidly with distance from the nitrogen atom.

With Ca^{++} montmorillonite deviations from theory were observed when the adsorption data were analysed in terms of either the "Langmuir" or the mass-action treatment with the exception of methyl-substituted ammonium compounds. These deviations have been attributed to the expansion or collapse of the interlamellar space on adsorption, resulting in either an enhanced or a restricted surface migration of the adsorbed cation in the interlamellar region.

In conjunction with adsorption studies the structure and orientation of the adsorbed molecule were investigated by X-ray diffraction and infra-red spectroscopy.

X-ray diffraction studies show that the alkylammonium cations studied were adsorbed as a one-layer complex by montmorillonite. The organic cations were adsorbed in an orientation so as to present their minimum thickness in the direction perpendicular to the clay surface. The observed contraction in the van der Waals thickness of the adsorbed molecule could be accounted for by "keying" of the cation into the hexagonal depressions of the silicate surface.

The infra-red spectra of the tetraalkylammonium cations adsorbed by montmorillonite indicate that the combined influence of the adsorption forces is not sufficient to produce a significant change in the molecular structure or conformations of the cations from those which occur in the chloride or bromide salts. As would be expected, the conformations of minimum thickness exist in the adsorbed phase.

The results reported in this thesis show that the presence of organic cations in the exchange complex of sodium and calcium montmorillonite markedly influences the hydration and swelling properties of the clay material. Although the mechanism of swelling of clays and clay-organic complexes has received considerable attention (Jordan, 1949; Norrish, 1954; Garrett and Walker, 1960; Aylmore and Quirk, 1959, 1960<u>b</u> and <u>c</u>; Weiss, 1963) it is only recently that attention has been focused on the adsorptive and swelling properties of clays containing both inorganic and organic cations (Emerson, 1962; Barrer and Brummer, 1963). It becomes apparent from the present study that "mixed" cationic clay systems show a markedly different swelling behaviour to that shown by the clay saturated with either inorganic or organic cations alone.

The effect of adsorbed organic cations on swelling is thought to arise from the fact that the relatively large and desolvated organic ion is able to disrupt the ordered water structures around the inorganic cations at the clay surface and hence modify the surface adsorption of water by cations. Posner and Quirk (1963) have suggested that it is this adsorption which provides the basic trigger mechanism for particle re-arrangement and the creation of a gel structure. Surface adsorption of water and its effect on particle re-arrangement and the formation of a gel framework are dependent on the size, adsorption affinity and other molecular properties of the adsorbed cations.

The adsorption of organic cations by montmorillonite appeared to occur in discrete layers within a single crystal rather than in a random fashion throughout the crystal. This phenomenon gave rise to random interstratification of sodium-rich and alkylammonium-rich layers within a single crystal when the parent material was a sodium clay (Barrer and Brummer, 1963). Since the sodium material gave extensive crystalline swelling in water $[d(001) > 30\ \text{Å}]$ whilst the complex saturated with alkylammonium cations did not expand beyond a basal spacing of 14 Å, diffuse double layers were probably absent in those layers within a crystal which were predominantly saturated with organic ions. As exchange of sodium for alkylammonium ions progressed an increasing number of layers within a given crystal became saturated with organic ions resulting in the collapse of diffuse double layers. This mechanism accounts for the observation that the water content of complexes showed a continuous and progressive decrease as the degree of surface coverage of the clay by alkylammonium cations increased. The rate of decrease in swelling was largest for the bigger alkylammonium ions. Large variations in the water content at pF 1.1 were also observed between complexes saturated with different alkylammonium cations, the smaller cations retaining the largest quantities of water. Since all of the alkylammonium ions showed limited crystalline swelling [d(001)< 20 Å], the variations in water content between cations must be due to differences in the structural arrangement of the clay particles and hence to differences in the amount of water retained within the gel structure. It seems probable that with the larger alkylammonium cations less interaction occurs between crystals so that there is only a limited amount of particle re-arrangement.

With the smaller cations a large hysteresis in the wetting and drying cycles was observed in the range between pF 1.1 and pF 4.2 indicating that considerable particle re-arrangement had occurred. This re-arrangement gives rise to an open gel structure. This behaviour contrasts with the virtual absence of appreciable swelling and hysteresis with large cations, when presumably the domain structure of the crystals was preserved (Aylmore and Quirk, 1960_a_). The relation between adsorption affinity and swelling can be seen from the observation that for alkylammonium cations which were adsorbed with a decrease in $\Delta G^m > 1000$ cals/mole, the rate of decrease in swelling as a function of surface coverage by the cations was identical and swelling reached a more or less constant value (water content 40 cc/100 g) when more than 1/3 of the total surface of the clay was covered by the cations.

When the parent clay is calcium saturated the presence of alkylammonium cations on the exchange complex has a dramatic effect on the water relationships of the complex. On the basis of hydration energy the adsorption of alkylammonium ions by calcium montmorillonite would be expected to result in a further decrease of the limited crystalline swelling shown by the calcium material [d(001) ≃ 19 Å]. It was observed, however, that as calcium is replaced by the smaller alkylammonium ions the swelling of the complexes rises to a maximum when calcium and alkylammonium ions are present in equal proportions, and then decreases. Much of the increase in swelling below half saturation by the organic cations can be attributed to interlamellar expansion associated with the formation of diffuse double layers on interlamellar surfaces. On the other hand, the progressive reduction in swelling when the maximum has been exceeded is probably due to the collapse of diffuse double layers on clay surfaces in a similar fashion to that for complexes with sodium montmorillonite.

The results of the present study suggest that the replacement of calcium ions by small alkylammonium cations in the interlamellar region of the crystal involves a release of energy, probably in the form of a net gain in entropy which enables the system to overcome the potential barrier of limited crystalline swelling shown by the clay saturated with either calcium or alkylammonium cations alone. It is likely that the organic cations were adsorbed in a desolvated state. This and the fact that the alkylammonium ion is larger than the calcium ion would disrupt the geometrical arrangement of the water molecules around the divalent calcium ion (Mathieson and Walker, 1954; Méring, 1946). This disruption of the ordered configuration of surface water gives rise to an increase in "structure-breaking" entropy (Frank and Evans, 1945).

Norrish (1954) has suggested that the absence of extensive crystalline swelling in calcium montmorillonite is due to the larger radius of dielectric saturation of the calcium ion as compared to that of the sodium ion. The disruption of the water structures around the interlamellar calcium ion by alkylammonium ions results in a decrease in the electrostatic attractive forces between the cation and the clay surface. Such a co-operative effect between two ions which individually only give limited crystalline swelling has not been previously reported and may provide a useful method in studying the interaction between ions and water in the vicinity of clay surfaces.

When the alkylammonium ion contains more than five carbon atoms the maximum in swelling is not observed. There is a progressive decrease in the water content of cores as the amount of organic ions present increases. The crystalline swelling of complexes with these large cations is limited in the entire range between zero to full saturation by the organic cation. It would appear that in this instance the gain in "structure-breaking" entropy was insufficient to overcome the attraction between cation and clay surface. This attraction becomes larger as the size of the cation increases. In addition, the increase in the number of hydrocarbon groups would render the cation more hydrophobic and hence surface adsorption of water by the cation is reduced.

It becomes apparent from the above analysis that detailed thermodynamic measurements on the interaction between ions at the clay surface are essential for a full understanding of the underlying mechanism of the swelling of "mixed" cationic clay systems. One major difficulty with such a system is to evaluate the relative contribution of attractive and repulsive forces between cation, water, and clay surface in an environment of changing dielectric.

The results reported in this thesis may have important practical implications in the area of the interaction between nutrient ions, water, and soil colloids under field conditions. It is known that the soil solution contains many different kinds of inorganic and organic cations. Each cation will compete for the clay surface and at any given time the exchange sites of the clay will be occupied by ions of different kind. Co-operative adsorption of cations will lead to random interstratification of layers within a single crystal and probably of crystals within a domain. This phenomenon will give rise to differential expansion of layers and crystals and hence to differences in nutrient availability to plant roots and in accessibility of adsorbed organic compounds to microbial organisms and extra-cellular enzymes.

The adsorption of organic cations by clays would also be expected to have an important effect on the physical properties of the soil. The replacement of the inorganic ions present on the clay surface by large organic cations results in a considerable decrease in the swelling of the clay. In addition, the hydrocarbon groups of the organic molecules will effectively repel water molecules and hence decrease the amount of gel water.

The mechanism whereby an uncharged linear polymer, in this instance polyvinyl alcohol, modifies the swelling of clays is different from that shown by simple organic cations. This difference arises from the fact that the adsorption of polyvinyl alcohol did not involve an ionic exchange mechanism, the polymer molecule being attached by a series of hydrogen bonds between the hydroxyl groups of the molecule and the surface oxygens of the clay (Emerson, 1956; Greenland, 1963). A further difference in the adsorption between polyvinyl alcohol and alkylammonium cations is that the former molecule due to its great length is able to form interparticle bonds.

Surface adsorption of water by cations at high pF remains unaltered but large swelling is physically resisted by the presence of cross-links in the complex as compared to the untreated clay material. The results show that the swelling of the clay-polymer complex is decreased as the amount of polymer present increases. This decrease in swelling, however, is not a simple function of the amount of polymer adsorbed. For a given amount of polymer adsorbed considerable variations in water content of complexes were observed. These variations are attributed to the relative frequency of interparticle bonding which is dependent on the initial clay/polymer solution ratio, the method of mixing of the polymer solution with the clay, the previous history of the clay, and the molecular weight of the polyvinyl alcohol. These observations can be explained in terms of the statistical probability that a polymer molecule becomes attached to several clay particles. This probability increases as the area available for adsorption and the length of free segments of the molecule increases. On the other hand, the frequency of interparticle bonding would be expected to decrease as the mean distance of separation between clay particles increases, that is, as the final suspension concentration decreases.

Suspension concentration does not appear to be the only factor determining the amount of swelling of the complex. The larger water contents for complexes formed by adding the polymer solution to a clay suspension as compared to complexes prepared by adding the solution to air-dry clay is attributed to the presence of an open gel structure in the former instance. When the polymer is added to an already aggregated clay system the molecule may spread over adjacent clay surfaces like a "coat of paint" (Greenland, 1963). This mechanism will strengthen the pore structure of the system and hence prevent the rapid uptake of water and the creation of an open gel structure. This explains the observation that polyvinyl alcohol introduced into air-dry clay aggregates prevents the aggregates from slaking when immersed in water.

It becomes apparent from the results obtained in this study that the practical application of synthetic soil conditioners to soils of poor structure must be evaluated in terms of many independent variables whose relative importance will depend on the particular set of conditions under consideration.

SUMMARY

The adsorption of homologous series of alkyl-substituted ammonium compounds by sodium and calcium montmorillonite has been studied.

Adsorption occurred by a cation exchange mechanism involving the replacement of an approximately equivalent amount of the inorganic cations initially present on the exchange complex.

The adsorption process could be treated either as a simultaneous competition between two cations for the exchange sites on the clay surface ("Langmuir" treatment) or as a heterogeneous ion-exchange equilibrium between the cations in solution and those in the clay phase.

The affinity or free energy of adsorption was a linear function of the molecular weight of the adsorbate. Variation in $-\Delta G^m$ between homologous series has been attributed to steric effects and the influence of hydrocarbon groups on the basicity of the alkylammonium compounds.

Evidence has been presented to show that adsorption occurred in discrete layers within a single crystal rather than in a random fashion throughout the crystal. This phenomenon gave rise to random interstratification of sodium- (or calcium-) rich and alkylammonium-rich layers within a single crystal (Barrer and Brummer, 1963).

X-ray diffraction and infra-red spectroscopy studies on the complexes between montmorillonite and alkylammonium compounds showed that the organic cations were adsorbed as a one-layer complex in an orientation so as to present their minimum thickness in the direction perpendicular to the clay surface. No significant change in the molecular conformation

of the adsorbed cations was observed as compared to those in aqueous solution. In regard to adsorption energetics the infra-red spectra of intercalated tetraalkylammonium cations yield no evidence to suggest that the conformations of the cations are influenced by compressive or crystal effects.

None of the alkylammonium ions studied gave extensive crystalline swelling $\left[d(001) > 30\ \text{Å}\right]$. This behaviour contrasts with the extensive crystalline swelling of vermiculite saturated with monobutylammonium ions reported by Garrett and Walker (1960).

There was a decrease in swelling of sodium montmorillonite as the amount of alkylammonium ions adsorbed increased. The decrease in swelling was associated more with the degree of surface coverage rather than with the degree of saturation of the exchange complex by the organic cations.

The limited crystalline swelling of calcium montmorillonite gave way to extensive crystalline swelling when about half of the cation sites were occupied by small alkylammonium ions (monoalkyl-, dimethyl-, trimethylammonium). Swelling of the complexes with these cations rose to a maximum when calcium and alkylammonium ions were present in approximately equal proportions, then decreased. When the alkylammonium ion contained more than five carbon atoms the maximum in swelling was not observed. For these large cations the crystalline swelling of the complexes was limited in the entire range between zero to complete saturation with the alkylammonium ions.

The swelling of complexes between montmorillonite and polyvinyl alcohol was dependent on the degree of interparticle bonding or cross-linking between clay crystals. The frequency of cross-linking was determined by the initial clay/polymer solution ratio, the method of mixing of the polymer solution with the clay, the previous history of the clay, and the molecular weight of the polymer. In addition to interparticle bonding the polymer molecule may spread over adjacent clay surfaces when added to an already aggregated clay system (Greenland, 1963). This mechanism would stabilize the aggregate further and hence prevent the rapid uptake of water.

Appendix I

Determination of the cation exchange capacity of the clay material.

The exchange capacity was determined by two procedures:

(i) By shaking the sodium and calcium clay suspension with normal ammonium acetate solution at pH 7, centrifuging and decanting the supernatant solution. This process was repeated 5 times. Excess electrolyte was removed by washing the clay material several times with 95 per cent ethanol. The ammonium retained by the clay was determined by steam distillation with MgO in a Markham still (see Appendix III).

(ii) By passing the sodium and calcium clay suspension down a column of the ammonium form of Amberlite I.R. 120 cation exchange resin. The clay eluate was made up to volume and aliquots were steam distilled as above. The amount of clay in the aliquot was determined by drying portions of the suspension in an electric oven at 105°C overnight.

The supernatant solutions of (i) were combined for subsequent estimation of sodium and calcium ions (see Appendix III) replaced by ammonium from the exchange complex.

The results of the cation exchange capacity determinations are summarized in Table 17.

Appendix I, contd.

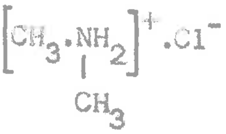
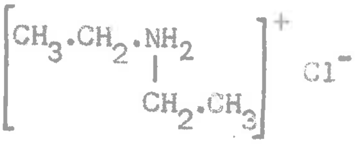
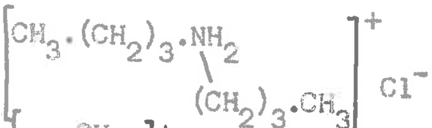
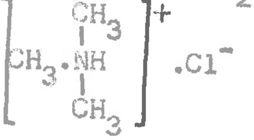
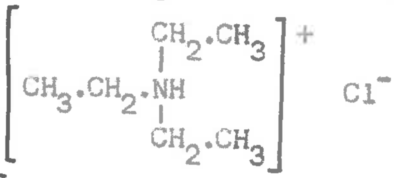
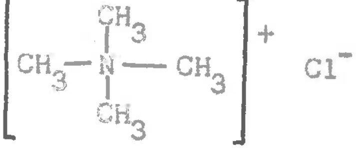
TABLE 17.

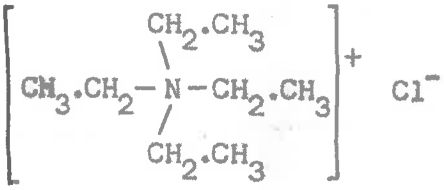
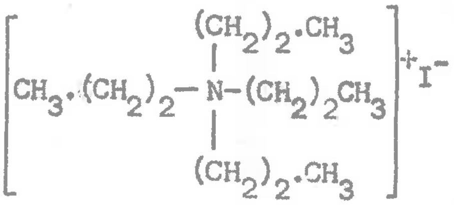
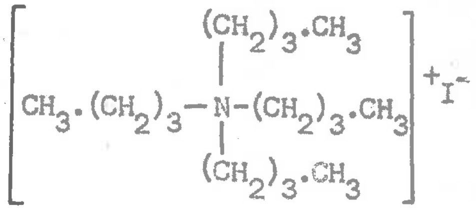
Cation exchange capacity of Redhill montmorillonite

Exchangeable cation	Sodium	Calcium
Cation exchange capacity by method (i), me/100g	89	94
Cation exchange capacity by method (ii), me/100 g	99	92
sodium replaced by method (i), me/100 g	86	3.4
calcium replaced by method (i), me/100 g	2.2	92.1

Appendix II

Sources of supply, structural formulae and purity checks of compounds studied.

	Compound	Structural formula	Source of supply
1.	Monomethylamine hydrochloride (monomethylammonium chloride)	$[CH_3.NH_3]^+.Cl^-$	Fluka AG Chemische Fabrik
2.	Monoethylamine hydrochloride (monoethylammonium chloride)	$[CH_3.CH_2.NH_3]^+.Cl^-$	"
3.	Mono-n-propylamine hydrochloride (mono-n-propylammonium chloride)	$[CH_3.(CH_2)_2.NH_3]^+.Cl^-$	"
4.	Mono-n-butylamine hydrochloride (mono-n-butylammonium chloride)	$[CH_3.(CH_2)_3.NH_3]^+.Cl^-$	"
5.	Dimethylamine hydrochloride (dimethylammonium chloride)	 $\left[\begin{array}{l}CH_3.NH_2\\ \qquad \vert\\ \qquad CH_3\end{array}\right]^+.Cl^-$	"
6.	Diethylamine hydrochloride (diethylammonium chloride)	 $\left[\begin{array}{l}CH_3.CH_2.NH_2\\ \qquad\qquad \vert\\ \qquad\qquad CH_2.CH_3\end{array}\right]^+ Cl^-$	"
7.	Di-n-butylamine hydrochloride (di-n-butylammonium chloride)	 $\left[\begin{array}{l}CH_3.(CH_2)_3.NH_2\\ \qquad\qquad\quad \backslash\\ \qquad\qquad\quad (CH_2)_3.CH_3\end{array}\right]^+ Cl^-$	Eastman Kodak
8.	Trimethylamine hydrochloride (trimethylammonium chloride)	 $\left[\begin{array}{l}\qquad CH_3\\ \qquad \vert\\ CH_3.NH\\ \qquad \vert\\ \qquad CH_3\end{array}\right]^+.Cl^-$	Fluka AG Chemische Fabrik
9.	Triethylamine hydrochloride (triethylammonium chloride)	 $\left[\begin{array}{l}\qquad\qquad CH_2.CH_3\\ \qquad\qquad \vert\\ CH_3.CH_2.NH\\ \qquad\qquad \vert\\ \qquad\qquad CH_2.CH_3\end{array}\right]^+ Cl^-$	"
10.	Tetramethylammonium bromide	 $\left[\begin{array}{c}CH_3\\ \vert\\ CH_3 - N - CH_3\\ \vert\\ CH_3\end{array}\right]^+ Cl^-$	British Drug Houses

Compound	Structural formula	Source of supply
11. Tetraethylammonium bromide	 $\left[\mathrm{CH_3.CH_2{-}\overset{CH_2.CH_3}{\underset{CH_2.CH_3}{N}}{-}CH_2.CH_3}\right]^{+}\mathrm{Cl}^{-}$	British Drug Houses
12. Tetra-n-propylammonium iodide	 $\left[\mathrm{CH_3.(CH_2)_2{-}\overset{(CH_2)_2.CH_3}{\underset{(CH_2)_2.CH_3}{N}}{-}(CH_2)_2CH_3}\right]^{+}\mathrm{I}^{-}$	Eastman Kodak
13. Tetra-n-butylammonium iodide	 $\left[\mathrm{CH_3.(CH_2)_3{-}\overset{(CH_2)_3.CH_3}{\underset{(CH_2)_3.CH_3}{N}}{-}(CH_2)_3.CH_3}\right]^{+}\mathrm{I}^{-}$	"

The purity of the compounds was checked by running a one-way paper chromatogram on Whatman No. 1 paper, using butanol-acetic acid - water as solvent (Lederer and Lederer, 1953, p. 134). For the monoalkylamine hydrochlorides a ninhydrin solution in acetone was used to develop the colour, whilst for the other compounds, Dragendorff's reagent was more satisfactory (Block, Durrum, and Zweig, 1958, p. 164).

The chromatogram showed that the compounds ran as a single spot. Minute amounts (<1 per cent) of impurities were present in monomethylamine hydrochloride. The compounds were used as received.

Appendix III

Quantitative methods for the estimation of inorganic and alkylammonium cations in solution.

(i) Estimation of sodium, potassium, and cesium

Sodium, potassium, and cesium ions in solution were determined by flaming an aliquot of the supernatant liquid, after appropiate dilution, in an EEL flame photometer. The alkylammonium ions did not interfere with the determination.

(ii) Estimation of calcium

Calcium ions in solution were determined by titrating aliquots against standard solution of the disodium salt of ethylenediamine tetraacetic acid (E.D.T.A.) at pH 10 in the presence of eriochrome black indicator.

(iii) The modified Kjeldahl technique for nitrogen estimation

Aliquots of the tetraalkylammonium solutions (1-5 ml) were digested with 5 ml of concentrated sulphuric acid in the presence of 1 g of a mixed catalyst (K_2SO_4-$CuSO_4$-Se, in the ratio of 100:10:1 by weight) contained in a 50 ml round-bottom Kjeldahl flask. The contents were digested for 3 hours on a "Gilmer" simmerstat electric heater. After cooling in air, the flasks were placed in a beaker containing crushed ice. This procedure was found effective in preventing violent reaction on addition of NaOH to the digest prior to distillation. The ice-cooled contents of the flasks were transferred to a Markham still with 5-10 ml water through the inlet funnel, followed with ± 20 ml of 40 % NaOH. The ammonia liberated is steam distilled off, absorbed into 5 ml of 4 per cent boric acid, collecting about 50 ml of distillate. The ammonium borate was titrated against standard HCl in the presence of a mixed bromcresol green-methyl red indicator (1 : 3 mixture in 0.1 per cent solution of methanol).

Before use the still was calibrated by steam distilling a known volume of standard NH_4Cl solution. Recovery of nitrogen was better than 99 per cent.

The mono-, di-, and trialkylammonium compounds were steam distilled as described above without prior digestion.

Appendix IV

Details of basal spacing results of complexes with inorganic and alkylammonium cations for different amounts adsorbed.

Na^+ montmorillonite

Cation	Amount adsorbed, me/100 g.	Basal spacing, Å	
		Moist	Oven-dry (70°C)
$Pr_1NH_3^+$	50.8	d	12.0
	55.8	d	12.2
	58.9	d	12.6
	63.5	13.2	12.7
	76.8	13.2	12.7
$Bu_1NH_3^+$	56	d	12.75
	60.2	13.5	12.75
	66.9	13.5	12.75
	77.5	13.5	12.75
$Me_2NH_2^+$	32.5	d	12.2
	41	d	12.3
	58.6	d	12.3
	69	d	12.75
	89	12.85	12.75

Appendix IV, contd. Na^+ montmorillonite

Cation	Amount adsorbed, me/100 g.	Basal spacing, Å Moist	 Oven-dry (70°C)
$Et_2NH_2^+$	49.9	d	12.7
	60.1	13.15 (b)	12.9
	68.6	13.15	13.0
	86.7	13.15	13.0
$Bu_2NH_2^+$	24.1	d	12.75 (b)
	34.8	13.2 (b)	12.8 (b)
	43.7	13.2 (b)	13.0
	54.1	13.3	13.1
	63.7	13.5	13.2
	78	13.5	13.2
	86.6	13.5	13.2
Me_3NH^+	43.5	d	12.4
	51	d	12.6
	63.9	d	12.8
	72.7	13.7	13.3
	84.1	13.7	13.4
Et_3NH^+	50	d	13.1
	62.4	13.15	13.15
	70.8	13.15	13.15
	86.7	13.15	13.15

Appendix IV, contd.

Na^+ montmorillonite

Cation	Amount adsorbed, me/100 g.	Basal spacing, Å	
		Moist	Oven-dry (70°C)
Me_4N^+	29.7	d	12.75
	45.	12.6	13.8
	57.3	13.75	13.8
	66.3	13.75	13.8
	73.3	13.75	13.8
	78.7	13.75	13.8
	85.6	13.75	13.8
Et_4N^+	22.7	d	12.75
	34.2	d	13.5
	46.2	13.75	13.75
	56.1	14.0	14.0
	70.3	14.0	14.0
	84.0	14.0	14.0
Pr_4N^+	15.9	d	12.75
	23	d	13.85
	34.5	d	14.5
	45	13.7	14.5
	57.8	14.7	14.5
	67.	14.7	14.3
	80.	14.7	14.5

Appendix IV, Contd. Na$^+$ montmorillonite

Cation	Amount adsorbed, me/100 g.	Basal spacing, Å Moist	Oven-dry (70°C)
Bu_4N^+	14	d	12.75
	26.9	15.30	13.3
	33.8	16.5	14.0
	47.2	16.5	14.7
	60.3	16.5	15.0
	73.1	16.5	15.1
	83.9	17.0	15.5
	95.9	17.0	16.30

Ca^{++} montmorillonite

Cation	Amount adsorbed, me/100 g.	Basal spacing, Å Moist	Oven-dry (70°C)
$Me_1NH_3^+$	14.6	18.7	12.75
	23.0	18.8	12.8
	54.6	d	12.2
	92.6	13.3 (b)	12.0
$Et_1NH_3^+$	9.8	18.8	12.75
	17.8	18.8	12.75
	27.1	18.8	12.6
	38.5	18.8	12.75
	56.1	d	12.6
	75.5	12.5	12.6
	84.9	12.5	12.6

Appendix IV, contd. Ca^{++} montmorillonite

Cation	Amount adsorbed, me/100g.	Basal spacing, Å	
		Moist	Oven-dry (70°C)
$Pr_1NH_3^+$	10.4	18.8	12.75
	22.0	18.3	12.7
	30.7	18.3	12.8
	36.2	d	12.8
	42.9	d	12.7
	69.8	13.7	12.7
	92.6	12.7	12.75
$Bu_1NH_3^+$	11.5	18.8	13.3
	23.9	18.7	12.65
	36.1	17.4	12.85
	43.0	d	12.85
	56.1	13.2 (b)	12.75
	75.1	12.85	12.75
$Me_2NH_2^+$	12.2	18.7	13.75
	20.4	18.7	13.50
	32.1	18.7	13.7
	40.0	18.7	13.5
	69.9	d	11.8
	89.3	12.35	12.2

Appendix IV, contd. Ca^{++}montmorillonite

Cation	Amount adsorbed, me/100 g.	Basal spacing, Å	
		Moist	Oven-dry (70°C)
$Et_2NH_2^+$	14.5	18.8	12.85
	21.2	18	12.85
	42.4	d	12.8
	48.1	d	12.8
	60.1	12.8 (b)	12.8
	70.9	12.8	12.8
$Bu_2NH_2^+$	11.8	18.3	
	24.1	16.3	
	34.5	14.2	
	42.7	13.75	
	54.8	13.2	
	67.3	13.2	
	84.4	13.2	
Me_3NH^+	15.8	18.8	12.6
	28.5	18.6	12.2
	40	18.3 (b)	12.6
	51.5	d	12.0
	57.9	d (14.9)	12.0
	75	12.75	12.3

Appendix IV, contd. Ca^{++} montmorillonite

Cation	Amount adsorbed, me/100 g.	Basal spacing, Å Moist	 Oven-dry (70°C)
Et_3NH^+	10.4	18.8	14.2
	19.9	18.3	14.2
	30.3	17.7 (b)	14.2
	39.8	13.2	12.85
	49.2	13.0	12.85
	57.8	12.85	12.85
	76.6	12.85	12.85
Me_4N^+	5.0	18.8	12.6
	12.0	18.8	12.75
	22.0	18.8	13.75
	39.0	16.3	13.5
	48.0	14.3	13.5
	55.1	13.75 (b)	13.5
	60.9	13.75	13.7
	84.0	13.75	13.5
Et_4N^+	5.0	18.1	13.25
	12.2	18.0	13.5
	24.1	15.8	13.75
	36.2	14.8	13.75
	47.6	13.75	13.75
	67.8	13.75	13.75
	80.7	13.75	13.75

Appendix IV, contd. Ca^{++} montmorillonite

Cation	Amount adsorbed, me/100 g.	Basal spacing, Å	
		Moist	Oven-dry (70°C)
Bu_4N^+	8.8	16.8	13.5
	17.5	16.5	13.5
	25.6	15.75	14.0
	41.3	15.5	13.75
	54.1	15.75	13.75
	65.1	15.75	13.75
	85.3	16.0	14.7
Na^+	5.0	19.0	14.0
	9.5	19.0	13.2
	17.5	19.0	12.3
	29.5	19.0	12.3
	45	d	-
	55	d	9.8
	70	d	9.8
K^+	11.0	18.8	13.2
	16.5	19.0	13.7
	25.0	19.0	13.8
	34.0	19.0	13.7
	45.0	d	-
	70	d	10.2
	80	d	10.2

Appendix IV, contd. Ca^{++} montmorillonite

Cation	Amount adsorbed, me/100 g.	Basal spacing, Å Moist	Basal spacing, Å Oven-dry (70°C)
NH_4^+	6.3	19.3	13.2
	10.6	19.3	13.7
	17.5	19.3	13.2
	28.7	19.7	12.75
	33.2	20.0	12.75
	52.7	d	12.0
	76.6	d	11.7
	87.8	d	11.6
Cs^+	7.0	19.0	12.75
	15.0	19.0	13.75
	30.0	19.0 (b)	13.75
	42.5	d	12.2
	52	d	12.2
	61	14.5 (b)	12.0
	95	12.2	12.0

Legend to Appendix IV.

d = diffuse

(b)= broad

Appendix V.

Method for the estimation of the mean number of lamellae per crystal (packet) for complexes of Ca^{++} montmorillonite containing different amounts of monoalkylammonium cations.

The thickness t of the crystal (packet) was obtained from the Scherrer formula which is of the form

$$t = \frac{S\lambda}{B \cos \alpha} \qquad \ldots\ldots(43)$$

where S is a constant equal to 51, λ is the wavelength ($CoK\alpha$ = 1.79 Å), and α is the Bragg angle in degrees. B is the width of the diffraction maximum in degrees of 2α at a half of the maximum intensity (I_{max}).

The number of lamellae per crystal (L) is given by the relationship

$$L = t/d(001) \qquad \ldots\ldots(44)$$

where d(001) is the basal spacing in Ångstrom units.

The method of calculating L is illustrated by the following example, for complexes with mono-n-butylammonium cations.

Appendix V, contd.

Amount adsorbed, (me/100 g)	α (degree)	cos α	I_{max}	B (degree)	t	d(001) (Å)	L
2.70	2.725	0.9989	84	1.50	60.92	18.8	3.24
11.50	2.725	0.9989	90	2.10	43.52	18.8	2.31
23.85	2.75	0.9989	45	2.50	36.56	18.7	1.96
31.19	2.90	0.9987	26	2.60	35.16	17.7	1.99
36.10	2.95	0.9986	36	2.70	33.85	17.6	1.92
49.54	3.90	0.9977	32	3.10	29.52	13.2	2.24
56.06	3.90	0.9977	32	1.70	53.82	13.2	4.08
75.03	4.0	0.9976	57	1.40	65.37	12.8	5.11
88.93	3.95	0.9976	88	1.0	91.50	12.85	7.12

Appendix VI

Surface coverage by alkylammonium cations for different amounts adsorbed onto Na^+ montmorillonite. In deriving surface coverage the edge areas of the montmorillonite crystals have been assumed to be negligibly small as compared to the total basal areas. In addition, the exchange sites on the clay surface were assumed to be uniformly distributed over the entire (interlamellar and external crystal) surface.

Cation	Amount adsorbed, me/100 g	θ_r	Cation	Amount adsorbed, me/100 g	θ_r
$Me_1NH_3^+$	9.92	0.018	$Et_1NH_3^+$	11.22	0.037
	19.86	0.036		21.19	0.071
	29.47	0.054		30.83	0.103
	38.22	0.070		38.38	0.128
	44.63	0.082		44.44	0.148
	49.83	0.091		51.14	0.170
	53.75	0.098		56.23	0.187
	57.10	0.104		59.39	0.198
	62.35	0.114		63.03	0.210
	75.77	0.138		76.94	0.256

Cation	Amount adsorbed, me/100 g	θ_r	Cation	Amount adsorbed, me/100 g	θ_r
$Pr_1NH_3^+$	9.57	0.039	$Bu_1NH_3^+$	10.31	0.047
	20.53	0.083		18.99	0.086
	30.60	0.123		28.05	0.127
	38.40	0.155		35.96	0.163
	45.50	0.183		42.86	0.194
	50.80	0.204		51.27	0.232
	55.80	0.225		55.97	0.254
	58.92	0.237		60.25	0.273
	63.54	0.256		66.90	0.303
	76.78	0.310		77.50	0.351

Appendix VI, contd.

Cation	Amount adsorbed, me/100 g.	θ_r	Cation	Amount adsorbed, me/100 g.	θ_r
$Me_2NH_2^+$	11.31	0.038	$Et_2NH_2^+$	10.86	0.050
	22.64	0.077		22.12	0.103
	32.45	0.110		33.30	0.157
	40.99	0.139		42.14	0.196
	47.80	0.163		49.91	0.232
	52.41	0.178		55.13	0.256
	58.64	0.199		60.05	0.279
	62.0	0.211		63.93	0.297
	68.91	0.234		68.61	0.319
	81.43	0.277		81.93	0.381
	88.97	0.302		86.71	0.403
	95.74	0.325			

Cation	Amount adsorbed, me/100 g.	θ_r	Cation	Amount adsorbed, me/100 g.	θ_r
$Bu_2NH_2^+$	4.0	0.033	Me_3NH^+	11.70	0.049
	11.34	0.093		23.09	0.097
	24.07	0.197		33.64	0.142
	34.75	0.284		43.53	0.183
	43.72	0.358		50.99	0.215
	54.66	0.447		58.39	0.246
	61.16	0.501		63.91	0.269
	66.53	0.545		67.90	0.286
	69.73	0.571		72.66	0.306
	77.98	0.638		84.12	0.354
	86.64	0.709		91.14	0.384
	90.69	0.742			

Appendix VI, contd.

Cation	Amount adsorbed, me/100 g.	θ_p	Cation	Amount adsorbed, me/100 g.	θ_r
Et_3NH^+	11.16	0.055	Me_4N^+	6.18	0.026
	21.61	0.107		13.92	0.06
	31.92	0.158		29.71	0.128
	41.96	0.208		45.01	0.194
	49.84	0.247		51.82	0.223
	56.21	0.278		57.34	0.246
	62.40	0.309		63.18	0.272
	64.96	0.321		66.28	0.285
	70.81	0.350		71.68	0.308
	80.50	0.398		73.25	0.315
	86.67	0.429		78.0	0.336
				78.74	0.339
				81.64	0.351
				85.64	0.368

Cation	Amount adsorbed, me/100 g.	θ_r	Cation	Amount adsorbed, me/100 g.	θ_r
Et_4N^+	10.71	0.067	Pr_4N^+	15.91	0.170
	22.71	0.142		22.97	0.245
	34.18	0.214		29.62	0.316
	46.19	0.288		34.48	0.368
	52.89	0.330		38.06	0.407
	56.14	0.350		45.0	0.481
	66.12	0.413		52.75	0.563
	70.34	0.439		57.78	0.617
	74.84	0.467		61.97	0.662
	76.92	0.480		67.01	0.716
	77.59	0.485		72.40	0.773
	83.98	0.524		79.66	0.851
	91.22	0.569		88.45	0.944
	93.22	0.582			

Appendix VII

Water content of cores in equilibrium with hydrostatic suctions of 100 cm (pF 2.0) and 700 cm (pF 2.8) for Na^+ and Ca^{++} montmorillonite containing different amounts of alkylammonium and monovalent inorganic cations.

Na^+ montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm	100 cm
$Me_1NH_3^+$	9.92	234	629
	19.86	214	635
	29.47	219	662
	38.22	181	623
	44.63	157	575
	49.83	154	591
	53.75	131	547
	57.10	121	556
	62.35	98	505
	75.77	65	236

Appendix VII, contd. Na^+ montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm	100 cm
$Et_1NH_3^+$	11.22	235	609
	21.19	219	610
	30.83	206	637
	38.38	185	618
	44.44	164	602
	51.44	160	583
	56.23	117	554
	59.39	111	552
	63.03	88	491
	76.94	58	388
$Pr_1NH_3^+$	9.57	257	694
	20.53	243	724
	30.60	204	756
	38.40	213	749
	45.50	161	727
	50.80	131	677
	55.80	117	670
	58.92	89	595
	63.54	68	572
	76.78	50	319

Appendix VII, contd.

Na^+ montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm	100 cm
$Bu_1NH_3^+$	10.31	245	651
	18.99	215	692
	28.05	204	684
	35.96	164	651
	42.86	115	610
	51.27	91	556
	55.97	70	538
	60.25	61	531
	66.90	49	310
	77.50	40	177
$Me_2NH_2^+$	11.13	277	687
	22.64	272	715
	32.45	243	698
	40.99	225	674
	47.80	219	620
	52.41	156	558
	58.64	134	522
	62.0	124	499
	68.91	89	399
	81.43	50	157
	88.97	49	124

Appendix VIII, contd. Na^+ montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm	100 cm
$Et_2NH_2^+$	10.86	232	601
	22.12	195	515
	33.30	164	388
	42.14	115	243
	49.91	79	153
	55.13	57	105
	60.05	53	85
	63.93	47	73
	68.61	42	59
	81.93	36	48
	86.71	37	48
$Bu_2NH_2^+$	4.0	236	595
	11.34	189	438
	24.07	118	215
	34.75	72	111
	43.72	48	64
	54.66	39	47
	61.16	37	44
	66.53	35	42
	69.73	33	40
	77.98	32	38
	86.64	30	36
	90.69	29	34

Appendix VII, contd.

Na^+ montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content cc/100 g.	
		700 cm	100 cm
Me_3NH^+	11.70	279	685
	23.09	252	680
	33.64	183	672
	43.53	201	652
	50.99	165	568
	58.39	128	464
	63.91	101	325
	67.90	78	250
	72.66	63	137
	84.12	49	83
	91.14	47	61
Et_3NH^+	11.16	204	537
	21.61	154	378
	31.92	110	261
	41.96	75	136
	49.84	50	77
	56.21	40	56
	62.40	37	48
	64.96	34	43
	70.81	32	38
	80.50	28	33
	86.67	29	33

Appendix VII , contd. Na^+ montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm	100 cm
Me_4N^+	6.18	233	482
	13.92	272	439
	29.71	175	346
	45.01	128	247
	51.82	121	208
	57.82	89	150
	63.18	78	126
	66.28	67	96
	71.68	62	85
	73.25	59	80
	78.0	57	74
	78.74	57	73
	81.64	52	63
	85.64	51	63

Appendix VII, contd. Na^+ montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm	100 cm
Et_4N^+	10.71	172	392
	22.71	134	274
	34.18	87	146
	46.10	60	87
	52.89	53	68
	56.14	45	53
	66.12	42	46
	70.34	36	39
	74.84	33	37
	76.92	35	35
	77.59	31	34
	83.98	29	33
	91.22	29	33
	93.22	29	33

Appendix VII , contd. Na^+ montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm	100 cm
Pr_4N^+	15.19	142	284
	22.97	112	210
	29.62	84	140
	34.48	73	110
	38.06	71	108
	45.0	54	74
	52.75	47	60
	57.78	46	57
	61.97	39	48
	67.01	40	47
	72.40	37	45
	79.66	38	42
	88.45	38	42

Appendix VII , contd. Na^+ montmorillonite.

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm	100 cm
Bu_4N^+	6.97	145	265
	13.95	99	153
	20.12	75	103
	26.94	63	78
	33.77	55	65
	40.64	47	57
	47.17	46	53
	53.71	46	51
	60.33	41	49
	64.85	40	45
	73.10	40	41
	79.97	39	40
	83.92	39	40
	95.90	39	40

Untreated Na^+ montmorillonite gave a water content of 270 cc/100 g at 700 cm and 630 cc/100 g at 100 cm (see Figure 19).

Appendix VII , contd. Ca^{++} montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm	100 cm
$Me_1NH_3^+$	2.59	82	131
	5.49	83	138
	10.92	84	163
	14.58	89	197
	21.01	91	212
	23.0	93	217
	25.58	95	245
	27.78	96	299
	29.26	98	303
	33.24	97	320
	45.0	107	-
	54.61	85	368
	86.5	82	264
	92.63	60	149

Appendix VII, contd. Ca^{++} montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g. 700 cm	100 cm
$Et_1NH_3^+$	5.39	87	125
	9.85	88	132
	13.24	92	144
	17.79	95	149
	19.51	93	162
	24.73	100	183
	27.06	100	197
	29.72	103	221
	38.50	95	264
	56.10	93	335
	75.50	71	217
	84.85	68	165
$Pr_1NH_3^+$	5.27	81	134
	10.41	88	140
	14.13	87	147
	18.0	96	179
	21.97	98	192
	25.48	99	209
	30.66	95	209
	36.22	93	249
	42.92	99	239
	69.81	69	244
	92.60	51	122

Appendix VII, contd.

Ca^{++} montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm	100 cm
$Bu_1NH_3^+$	2.70	45	124
	6.06	82	125
	11.50	85	132
	16.86	86	162
	23.85	96	185
	31.19	101	206
	36.10	101	219
	43.03	105	252
	49.54	106	233
	56.06	109	182
	75.03	93	97
	88.93	57.5	61
$Me_2NH_2^+$	6.72	84	144
	12.15	88	160
	16.63	91	194
	20.38	92	235
	24.27	93	248
	29.49	95	284
	32.14	88	236
	35.30	91	245
	39.97	83	292
	69.86	61	150
	89.27	52	105
	98.41	49	96

Appendix VII Contd. Ca^{++} montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm	100 cm
$Et_2NH_2^+$	7.55	80	123
	14.45	77	135
	21.21	74	122
	26.69	66	110
	34.76	63	97
	42.38	56	90
	48.13	54	83
	53.33	50	74
	60.07	47	66
	70.89	40	51
	75.11	39	46
	99.0	37	43
$Bu_2NH_2^+$	4.5	77	104
	11.84	69	88
	24.09	56	70
	34.50	47	53
	42.73	40	43
	50.07	35	38
	54.84	33	36
	56.74	33	35
	58.28	31.5	34
	67.33	31	34
	84.39	29	32
	91.70	28	31.5

Appendix VII, contd.

Ca^{++} montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm	100 cm
Me_3NH^+	8.46	85	132
	15.80	87	152
	22.77	87	176
	28.51	90	206
	34.10	90	217
	40.0	91	230
	44.05	89	269
	51.45	87	266
	57.93	84	169
	75.0	65	119
	100.0	57	69
Et_3NH^+	10.35	73	111
	19.89	65	100
	30.26	58	86.5
	39.82	53	73
	49.18	46	60
	54.28	32	35
	57.53	20	50
	57.80	39	45
	66.80	36	41
	76.63	37	40
	87.0	32	33

Appendix VII, contd. Ca^{++} montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm.	100 cm.
Me_4N^+	4.98	88	127
	11.96	90	135
	22.03	92	136
	30.78	89	128
	38.95	83	125
	47.95	77	109
	55.10	72	101
	60.89	69	87
	65.55	64	86
	71.13	64	77
	83.99	58	70
	90.12	55	68
Et_4N^+	4.97	70	121
	12.19	59	115
	24.10	48	97
	36.23	43	81
	47.59	39	63
	55.45	38	48
	61.07	36	42
	64.89	35	39
	67.83	34	36
	72.21	35	35
	80.71	33	32
	90.28	35	31

Appendix VII, contd. Ca^{++} montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm.	100 cm.
Bu_4N^+	8.76	83	93
	17.47	79	70
	25.58	70	56
	34.0	64	50
	41.33	53	44
	48.02	43.5	42
	54.05	39.5	41
	59.02	38	36.5
	65.08	36	38
	66.75	35	37
	85.30	33	37
	104.20	33	37.5

Untreated Ca^{++} montmorillonite gave a water content of 80 cc/100 g at 700 cm and 120 cc/100 g at 100 cm (see Figure 19).

Appendix VII, contd. Ca^{++} montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm	100 cm.
Na^+	2.5	87	116
	5.	89	123
	9.5	92	139
	15.	96	160
	17.5	101	176
	20.5	104	192
	29.5	118	282
	45	165	405
	55	188	455
	60	207	491
	70	235	531
K^+	6.75	88	130
	11.	90	140
	16.5	94	147
	22.	96	160
	25.	100	172
	34.	101	188
	45.	112	245
	70.	140	331
	80.	148	359
	85.	157	367

Appendix VII, contd. Ca^{++} montmorillonite

Cation	Amount adsorbed, me/100 g.	Water content, cc/100 g.	
		700 cm	100 cm.
NH_4^+	6.27	85	117
	10.64	87	126
	17.54	90	139
	23.54	95	157
	28.66	97	166
	33.19	100	185
	52.72	111	249
	76.60	127	303
	87.77	128	298
	93.72	123	285
Cs^+	7.	84	123
	15	85	124
	30	84	126
	42.5	76	113
	52	67	97
	61	56	83
	88	48	67
	95	49	63

Appendix VIII

Determination of the negative adsorption of chloride ions by complexes of Na^+ montmorillonite containing different amounts of tetraalkylammonium cations.

About 0.2 g of the air-dry complex was weighed out accurately into tared stoppered polypropylene centrifuge tubes of 50 ml capacity. To each tube was added 10 ml of 0.01 N NaCl solution. The tubes were shaken overnight on the end-over-end mechanical shaker in a constant temperature room, maintained at 25 ± 0.5 °C and centrifuged. The supernatant liquid was poured into a tared titration flask and weighed. The tube containing the clay and entrained liquid was also weighed. The chloride content of the supernatant liquid and that of the entrained solution was determined by potentiometric titration against standard $AgNO_3$ solution by the method of Kolthoff and Kuroda (1951) with a modified electrode which was

Platinum / Quinhydrone in phthalate buffer, pH 3.2 / Saturated KNO_3 / Ag / AgCl

used with a Cambridge pH meter.

The amount of negatively adsorbed chloride ions was found by difference between the chloride content of the supernatant liquid and that of the entrained solution. This amount was expressed as a volume from which chloride was completely excluded per unit weight of clay.

Appendix IX.

Water vapour sorbed at different relative humidity (P/P_o) by Na^+ and Ca^{++} montmorillonite and their complexes with alkylammonium cations.

	Na^+ montmorillonite		Ca^{++} montmorillonite	
P/P_o (%)	Adsorption (cc/100 g)	Desorption (cc/100 g)	Adsorption (cc/100 g)	Desorption (cc/100 g)
15	3.23	6.03	7.78	7.81
19	5.86	8.67	9.80	10.85
33	7.50	12.37	15.58	15.63
51	12.78	17.55	19.30	20.98
75	21.71	24.84	24.70	26.34
86	25.75	30.60	25.60	
96	44.24	52.98	40.0	47.47

Appendix IX, contd.

Complexes saturated with alkylammonium cations

$Na^+ \rightarrow Me_1NH_3^+$			$Na^+ \rightarrow Et_1NH_3^+$	
P/P_o (%)	Adsorption (cc/100 g)	Desorption (cc/100 g)	Adsorption (cc/100 g)	Desorption (cc/100 g)
15	3.98	6.03	3.43	4.29
19	5.25	6.30	4.53	6.04
33	8.26	9.35	6.77	8.84
51	10.87	13.21	10.08	12.62
75	14.57	17.39	13.07	16.84
86	17.21	19.85	16.19	19.40
96	23.43	32.84	21.21	32.26

Appendix IX, contd.

Complexes saturated with alkylammonium cations

	$Na^+ \rightarrow Pr_1NH_3^+$		$Na^+ \rightarrow Bu_1NH_3^+$	
P/P_o (%)	Adsorption (cc/100 g)	Desorption (cc/100 g)	Adsorption (cc/100 g)	Desorption (cc/100 g)
15	3.43	4.19	2.97	4.21
19	4.07	5.47	3.59	5.69
33	5.88	8.10	5.09	8.28
51	9.25	11.52	7.97	11.91
75	12.98	15.65	11.84	16.10
86	14.76	18.0	13.87	18.13
96	20.12	29.41	18.66	30.22

	$Na^+ \rightarrow Me_2NH_2^+$		$Na^+ \rightarrow Et_2NH_2^+$	
P/P_o (%)	Adsorption (cc/100 g)	Desorption (cc/100 g)	Adsorption (cc/100 g)	Desorption (cc/100 g)
15	3.63	4.33	2.77	3.0
19	4.41	5.75	3.64	3.88
33	7.07	8.69	5.35	5.92
51	10.14	12.46	8.17	9.53
75	14.25	16.0	11.76	13.08
86	16.10	19.04	14.17	15.25
96	21.74	29.76	19.09	23.27

Appendix IX, contd.

Complexes saturated with alkylammonium cations

$Na^+ \rightarrow Bu_2NH_2^+$ | | | $Na^+ \rightarrow Me_3NH^+$ |

P/P_o (%)	Adsorption (cc/100 g)	Desorption (cc/100 g)	Adsorption (cc/100 g)	Desorption (cc/100 g)
15	1.84	1.84	2.29	2.34
19	2.13	2.36	3.77	4.09
33	3.27	3.43	7.07	7.77
51	5.64	6.29	10.82	11.94
75	8.55	9.90	14.91	15.84
86	10.68	11.63	17.22	18.91
96	15.60	18.94	23.33	29.0

$Na^+ \rightarrow Et_3NH^+$ | | | $Na^+ \rightarrow Me_4N^+$ |

P/P_o (%)	Adsorption (cc/100 g)	Desorption (cc/100 g)	Adsorption (cc/100 g)	Desorption (cc/100 g)
15	1.48	1.46	4.62	4.64
19	1.95	2.09	6.04	6.10
33	3.67	3.92	8.68	8.94
51	6.59	7.76	11.85	12.90
75	10.52	11.34	15.31	17.28
86	12.61	13.59	18.69	20.35
96	17.28	20.93	25.07	31.20

Appendix IX, contd.

Complexes saturated with alkylammonium cations.

	$Na^+ \rightarrow Et_4N^+$		$Na^+ \rightarrow Pr_4N^+$	
P/P_o (%)	Adsorption (cc/100 g)	Desorption (cc/100 g)	Adsorption (cc/100 g)	Desorption (cc/100 g)
15	1.55	1.50	1.30	1.34
19	2.05	2.07	1.70	1.83
33	3.58	3.86	2.95	3.17
51	6.63	7.30	5.57	6.27
75	10.04	11.28	8.94	10.0
86	12.32	13.13	11.76	12.27
96	17.47	20.60	16.98	21.34

	$Na^+ \rightarrow Bu_4N^+$	
P/P_o (%)	Adsorption (cc/100 g)	Desorption (cc/100 g)
15	1.35	1.41
9	1.85	1.93
33	2.47	2.97
51	4.77	5.28
75	9.22	10.02
86	11.89	12.81
96	18.53	21.78

Appendix IX, contd.

Complexes containing different amounts of alkylammonium cations

Na^+ montmorillonite

Cation	Amount Adsorbed (me/100 g)	Water vapour adsorbed, cc/100 g.					
		P/P_o (%)					
		15	19	33	51	75	96
$Me_1NH_3^+$	29.47	3.90	5.61	8.90	14.15	18.54	39.39
	44.63	3.73	5.33	8.53	14.21	17.76	39.25
	53.75	4.19	5.90	9.0	14.13	17.39	38.97
$Et_1NH_3^+$	38.38	2.66	3.82	6.94	11.81	16.20	33.68
	56.23	2.76	3.98	6.96	11.60	15.36	34.70
$Pr_1NH_3^+$	30.60	2.14	3.35	6.57	11.93	16.76	36.73
	50.80	2.38	3.37	6.03	10.94	14.59	32.12
	63.54	2.86	3.64	5.85	10.40	13.65	28.35
$Bu_1NH_3^+$	28.05	2.14	3.13	6.09	12.01	17.43	37.66
	51.27	2.21	2.99	5.20	10.01	13.78	27.83
	66.90	2.82	3.43	5.33	9.56	12.75	25.25

Appendix IX, Contd.

Complexes containing different amounts of alkylammonium cations

Na^+ montmorillonite

Cation	Amount Adsorbed (me/100 g)	Water vapour adsorbed, cc/100 g.					
		P/P$_o$ (%)					
		15	19	33	51	75	96
$Me_2NH_2^+$	32.45	2.86	4.19	7.34	12.20	17.54	36.61
	52.41	3.17	4.49	7.53	12.55	16.51	34.08
	68.91	3.36	4.79	7.76	12.55	16.17	32.47
$Et_2NH_2^+$	33.30	2.64	3.79	6.43	10.91	15.38	32.84
	55.13	2.73	3.50	5.79	9.84	13.33	26.78
	68.61	2.55	3.36	5.37	9.39	12.35	24.56
$Bu_2NH_2^+$	24.07	1.96	3.01	5.90	10.61	15.20	30.80
	54.66	1.59	2.07	3.90	7.68	10.49	19.02
	69.73	1.63	2.07	3.26	6.41	8.91	17.28
Et_3NH^+	31.92	1.77	2.78	5.05	9.47	14.01	30.30
	56.21	1.11	1.73	3.46	7.30	10.52	24.38
	70.81	1.16	1.55	2.71	6.32	8.90	19.74

Appendix IX, contd.

Complexes containing different amounts of alkylammonium cations

Ca^{++} montmorillonite

Cation	Amount adsorbed (me/100 g)	Water vapour adsorbed, cc/100 g. P/P_o (%)				
		15	19	33	57	86
$Me_1NH_3^+$	2.59	5.69	8.11	13.66	16.64	25.46
	10.92	5.31	7.64	13.21	16.32	25.0
	21.01	4.81	7.04	11.78	14.85	23.43
	25.58	4.82	7.16	11.34	14.08	22.82
	29.26	4.59	6.89	11.35	13.78	22.57
	54.61	4.51	6.10	10.12	11.83	19.27
$Et_1NH_3^+$	5.39	6.05	8.50	14.41	17.15	25.94
	13.24	5.57	7.92	14.08	16.57	24.63
	19.51	5.47	7.61	13.08	15.35	22.96
	27.06	4.97	7.10	12.50	14.49	22.16
	38.50	4.71	6.70	11.54	13.52	20.60
	75.50	2.76	3.84	7.31	8.63	15.83

Appendix IX, contd.

Complexes containing different amounts of alkylammonium cations

Ca^{++} montmorillonite

Cation	Amount adsorbed me/100 g	Water vapour adsorbed, cc/100 g				
		P/P_o (%)				
		15	19	33	51	86
$Bu_1NH_3^+$	2.70	4.86	7.91	13.78	16.64	25.24
	11.50	4.81	7.14	12.64	15.25	23.76
	23.85	4.46	6.35	11.49	13.65	20.95
	36.10	3.89	5.56	10.29	11.96	18.50
	49.54	3.53	4.91	8.94	10.45	16.62
	75.03	2.33	3.43	6.73	7.71	13.46

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