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Title: SWELLING OF ALKYLAMMONIUM MONTMORILLONITES

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Adsorption on a series of primary n-alkylammonium bentonites was studied by simultaneous gravimetric determination of the adsorption isotherm and X-ray diffraction measurement of the c-spacing. All adsorbates gave typical Type II isotherms. BET plots were linear in the region $P/P_o = 0.10 - 0.35$ and v_m values were calculated. X-ray diffraction of the dry clay showed that the amine chains lay flat on the clay surface in two layers. Polar adsorbates, such as water, and nonpolar adsorbates, as n-heptane, did not cause any change in the c-spacing. However alcohols, adsorbates with both polar and nonpolar characteristics, caused a separation of the clay platelets to a distance corresponding to the calculated length of the amine ion, indicating that alcohol adsorption caused a rearrangement of the amine ions from their original prone position to an extended upright orientation. It was postulated that two adsorption processes were involved in the expansion, adsorption of the

polar portion of the alcohol molecule on the oxygen surface of the clay platelet, possibly by hydrogen bond formation, and van der Waals bonding between the nonpolar part of the alcohol molecule and the amine chain.

Adsorption of several other polar organic compounds was also satisfactorily explained. The effects of adsorbing polar and nonpolar compounds together was investigated and it was found that this also caused an expansion of the clay platelets.

Swelling of Alkylammonium Montmorillonites

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I. INTRODUCTION

Origin and Structure of Clay Minerals

The term clay has a variety of meanings. In general it refers to a natural, earthy, fine-grained material which develops plasticity when mixed with a limited amount of water. However in soil science the term is often used for the soil fraction with a diameter of less than 2μ, and in chemistry it refers to finely divided crystalline materials having a particular crystalline structure.

Clay materials are produced naturally in several ways. They may be formed by hydrothermal action and are often found as an aureole around ore deposits or associated with hot springs, geysers or fumaroles. They are found in soil due to the weathering of rocks such as volcanic matter. Or they may be found in sediments deposited on ocean floors, lake and river bottoms, or in glacial deposits.

Clay minerals are often found mixed with other minerals and organic matter. Difference in particle size is the basis for separating clay and nonclay materials with the clay fraction comprising the smallest particles. The best separation is usually obtained at 2μ, and for this reason 2μ is often taken as the upper limit of clay particle size. Chemical analysis of clays shows them to be essentially silica, alumina and water often with appreciable amounts of iron, alkalies and alkaline earths.

The idea that clay materials are composed of extremely small particles of a limited number of crystalline minerals is relatively old (41, 42). But it was not until about 1920 that adequate research tools, primarily X-ray diffraction analysis, were available to show that clay minerals are essentially hydrous aluminum silicates with magnesium or iron sometimes substituted for the aluminum. Some clays are composed of a single clay mineral but many are mixtures of two or more.

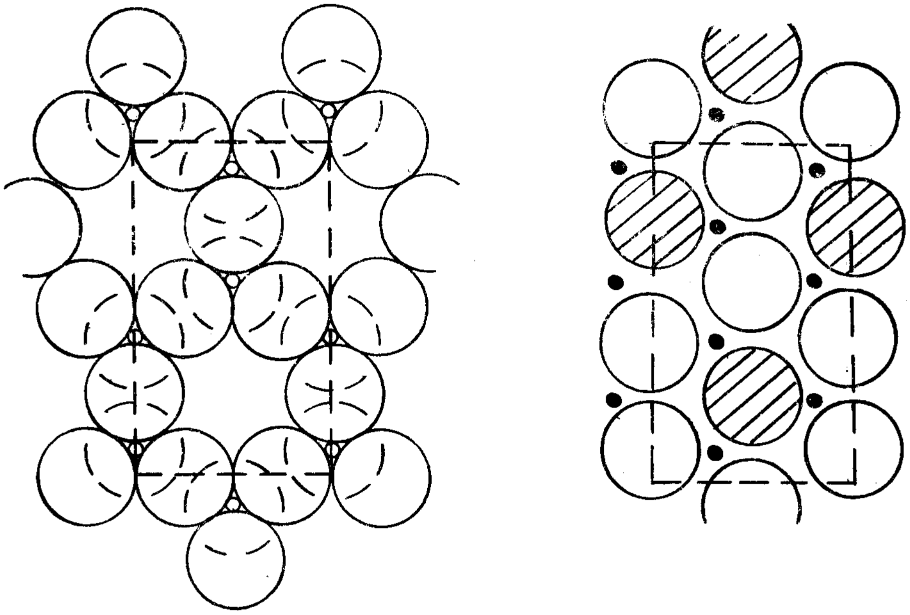
Following Pauling's models of layer silicates (58), the basic structures of most of the clays were determined in the 1930's (26, 27, 32).

The lattice of most clays involves two basic structural units: two-dimensional arrays of silicon-oxygen tetrahedra and two-dimensional arrays of aluminum-oxygen-hydroxyl octahedra. In the silicon-oxygen sheet, sometimes called the silica or tetrahedral sheet, the silicon atoms are coordinated with four oxygen atoms located at the vertices of a regular tetrahedron with the silicon atom in the center. Three of the four oxygen atoms are shared with three other tetrahedra. These shared oxygen atoms lie in a plane above the silicon atoms while the fourth unshared oxygen atom points downward. In the aluminum-oxygen-hydroxyl sheet, also called the alumina, octahedral or gibbsite sheet, the aluminum atoms are coordinated with six oxygen atoms or hydroxyl groups which are arranged around the aluminum atom at the vertices of a regular octahedron, three in a plane above the aluminum atom and three in a plane below. Each oxygen atom or hydroxyl group is shared with two other octahedra.

The almost identical dimensions of the tetrahedral and octrahedral sheets allow the sharing of oxygen atoms between the sheets. It can be seen that the unshared oxygen atoms of the silica sheet (dashed circles in Figure 1a) can be superimposed on the oxygen atoms of the alumina sheet. The octahedral positions which do not coincide with an oxygen atom in the silica sheet are occupied by hydroxyl groups (holes in Figure 1a). This sharing of oxygen atoms may occur between one silica and one alumina sheet to form the so-called "two-layer" minerals; or an alumina sheet may share oxygen atoms with two silica sheets, one on each side, to form the "three-layer" minerals. This combination of an octahedral sheet and one or two tetrahedral sheets will be referred to as a platelet.

The unit cell of the "three-layer" platelet is shown in Figure 2. In order for the unit cell to be electrically neutral, only four of the six possible octrahedral positions are occupied by aluminum atoms leaving a third of the positions vacant (compare Figures 1b and

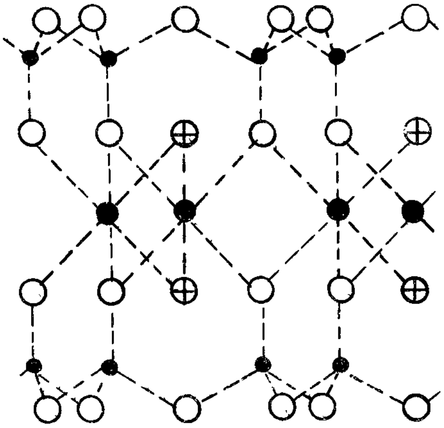
Figure 1. Structural units of clay minerals.
(Dotted lines; unit cell)



a. Tetrahedral sheet. b. Octahedral sheet.

○ Oxygen
▨ Hydroxyl
∘ Silicon
• Aluminum

Figure 2. Unit cell of pyrophylite
(Schematic)



6	O				−12
4	Si				+16
4	O	+	2	OH	−10
4	Al				+12
4	O	+	2	OH	−10
4	Si				+16
6	O				−12

2).

The dimensions of the unit cell, $a_o = 5.15Å$ and $b_o = 8.9Å$, can be determined by X-ray diffraction. The distance between a certain plane in one platelet and the corresponding plane in the next platelet is called the 001, basal or c-spacing. The determination of the c-spacing is a method for differentiating between "two-layer" minerals, $c = 7.2Å$, and "three-layer" minerals, $c = 9.2Å$. It can also be used to find the separation between platelets if the thickness of the platelets is known. This c-spacing is not necessarily the crystallographic c_o spacing since the platelets may not be stacked symmetrically.

The mineral pyrophyllite consists of stacks of the neutral "three-layer" platelets. The platelets are held together by van der Waals forces. Since these forces are very weak compared to the primary valence forces, cleavage parallel to the platelets is relatively easy and this mineral consequently occurs in the form of flakes. However these flakes are quite large, so pyrophyllite is not properly classified as a clay mineral.

The structure of pyrophyllite, though, is the prototype of many "three-layer" clay minerals including the montmorillonite group. It is possible for the aluminum and silicon atoms in the prototype structure to be replaced by other atoms; this is called isomorphic substitution. In the montmorillonite group, silicon atoms in the tetrahedral sheet are sometimes replaced by aluminum atoms, and in the octahedral sheet aluminum atoms may be replaced, with or without complete filling of the third vacant octahedral position, by magnesium, iron, chromium, zinc or lithium. Often this substitution results in a deficit of positive charge, or in other words, the platelet has a net negative charge. In order that the clay mineral may be electrically neutral, this negative charge is compensated by cations located on the surfaces of the platelets. The presence of these compensating cations between the platelets causes an increase in the c-spacing, for example from 9.13Å for pyrophyllite to 9.6Å for sodium montmorillonite and more for larger compensating cations. This increase for sodium montmorillonite is less than the ionic radius of sodium, 0.95Å, indicating that the sodium ions are partly sunk into the holes between the oxygen atoms of the surface.

In the presence of a salt solution, the compensating cations may be easily exchanged by the cations in the solution. The cation exchange capacity, CEC, is expressed in milliequivalents of exchangeable cations per 100 grams of dry clay. Thus the CEC is a measure of the amount of isomorphic substitution. The CEC of montmorillonites varies from 80 to 150 meq/100g.

Clay-Water System

When montmorillonite clays are exposed to water vapor the water molecules are adsorbed not only on the outer surfaces of the clay but also between the platelets, thus causing the platelets to expand and the c-spacing to increase. The presence of exchangeable cations is essential, and in general the amount of adsorption, dependent on the size and charge of these cations, increases with decreasing size and increasing charge.

Mooney, Keenan and Wood (50, 51), studying water vapor adsorption on sodium bentonite, measured the change in c-spacing as a function of the amount adsorbed. They observed that the hydration took place in a stepwise manner. As the amount of adsorption increased, spacings of 10Å, 12.5Å and 15.5Å were observed corresponding to the dry clay, one layer and two layers of water respectively. Stepwise hydration of montmorillonite has also been reported by Bradley, Grim and Clark (6) and Hofmann and Hausdorf (33).

It is probable, however, that the layers of water molecules are not arranged uniformly over the surface of the platelet but are clustered around the exchangeable cations forming a hydration sphere. Correlating the c-spacing with the amount of water adsorbed on calcium montmorillonite, Méring (49) postulated that the water molecules in the first two layers initially formed octahedral hydration spheres around the cations, then filled the remaining space. Norrish (53) has shown that the amount of swelling is related to the quantity U/v^2 where U is the hydration energy and v the charge on the cation; while Orchiston (54, 55, 56) found that the heats of hydration of exchangeable cations are linearily related to the heat of adsorption parameter of the BET equation. Quirk (59),using other people's data, has pointed out that the surface areas calculated from water adsorption using the BET equation, which assumes a uniform monolayer, vary depending on the cation and the surface charge density. Although there appears to be no conclusive X-ray evidence supporting this mechanism for water adsorption on montmorillonite, Mathieson and Walker (47) have used a and b-spacing data for vermiculite to show that the water molecules between the platelets of this clay are arranged in two sheets so as to provide octahedral coordination for the exchangeable magnesium ions which are located midway between the two water sheets.

Consequently it is thought that the mechanism of water adsorption involves the hydration of the exchangeable cations removing them from the cavities of the platelets, as well as adsorption of water molecules on the oxygen surface of the platelet by the formation of hydrogen bonds, or surface hydration. The energy released by these two processes is then sufficient to overcome the attractive forces between the platelets causing expansion.

The expansion process discussed so far does not affect the stacked arrangement of the platelets, only the distance between them. At 99% humidity, the clay adsorbs no more than 0.5g water/g clay and at most doubles its volume.

When the clay is brought in contact with the liquid, however, gelation occurs, that is, a homogeneous system is formed which possesses some rigidity and elasticity. Hydration and dissociation of the cations reduce their shielding effect and increase the repulsion between platelet surfaces. The platelets are no longer arranged in stacks but are linked by edge-to-face and edge-to-edge associations analogous to a "house-of-cards". This skeletal structure gives the gel its rigidity. When forming a gel, sodium montmorillonite, for example, takes up 10g water/g clay. The platelets are separated by 100Å (52) and the volume of the gel is 20 times the original volume of the clay.

Interaction of Clays and Organic Compounds

Organic compounds can be adsorbed between clay platelets either as neutral molecules or as ions replacing the exchangeable cations. This is usually done either by bringing the dry clay in contact with the organic liquid or vapor, or by mixing a clay-water suspension and the organic liquid. The organic compound adsorbed between the platelets causes an increase in the c-spacing which depends on the size of the organic molecule, the number of layers and the orientation.

Bradley (5) and Green-Kelly (22, 23, 24) have studied the variations in c-spacing with the adsorption of a wide variety of neutral organic molecules on montmorillonite. Saturated hydrocarbons such as n-heptane and cyclohexane cause no change in the c-spacing and are presumably not adsorbed between the platelets. However aromatic and polar compounds are adsorbed, displacing the water from the clay surfaces. In general, the energy of adsorption decreases as the nonpolar part of the molecule becomes larger. Usually only a single layer of molecules is formed, though in the case of highly polar substances multiple layers are formed.

MacEwan (43, 44), studying the variation in c-spacing with the adsorption of a series of primary alcohols, has explained the formation of multiple layers of highly polar molecules as follows: oxygen atoms comprise the surfaces of the clay platelet and behave as sheets of diffuse negative charge. Small polar molecules when adsorbed are oriented with their positive ends toward the clay surface. In this way, one layer will be adsorbed on each surface forming two layers between the platelets as observed for methanol and ethanol. For larger alcohols, the van der Waals forces, or C-H···O bonds as suggested by Bradley (5), between the nonpolar part of the molecule and the surface become more important. Since these forces are non-directional only one layer of adsorbed molecules is formed.

Barshad (4) observed the same spacings as MacEwan but found a rearrangement with nonanol and decanol to give spacings corresponding to the molecules standing upright. Since the dipole moment is essentially constant for this series of alcohols, he suggested that the rearrangement was related to the dielectric constant of the alcohol. Using mixtures of two liquids where the dielectric constant could be varied by changing the composition, he found the spacings reached a minimum at dielectric constants of about 20 and increased as the dielectric constant was increased or decreased. Consequently he proposed two competing roles of the dielectric constant: 1) a medium of high dielectric "shields" the platelets, decreasing the attractive forces between them; thus the expansion should be proportional to the dielectric constant, and 2) the lower the dielectric constant, the greater the attractive force between the surface and the solvent molecules; therefore the expansion, which is a measure of adsorption, should be inversly proportional to the dielectric constant. The first role is important when the forces between platelets are only slightly smaller than adsorption forces, but as the latter increase the second role becomes important.

Aragon, Ruiz and MacEwan (1) found that the adsorption of normal primary amine molecules on montmorillonite resulted in large c-spacings corresponding to a separation somewhat less than twice the length of the amine. They postulated that the methylene group adjacent to the amine group was arranged prone to the surface and the rest of the carbon chain vertical. Brindley (7) has pointed out that a 65° inclination of the extended chains would give the same spacings and also give a much more favorable geometry for hydrogen bonding of the amine group to the surface. It is also possible that the chains are in a cis-trans arrangement rather than a trans-trans arrangement (66).

So far, only the adsorption of neutral organic molecules has been discussed, in which case the compensating inorganic cations remain between the clay platelets. However some organic substances, such as amines, can be attached to clay surfaces either as molecules or as cations replacing the exchangeable inorganic cations. In the latter case the exchangeable inorganic cations become completely dissociated from the clay, while the organic ions become oriented on the clay surface with their positive charge balancing the negative charge of the clay platelet. In addition to this coulombic attraction, the hydrocarbon groups are held to the clay surface by van der Waals forces. The exchange is usually accompanied by the removal of any water present between the platelets and the transformation from a hydrophilic to a hydrophobic, or organophilic, surface. That is, the surface is now preferentially wet by an organic solvent in competition with water. In general, the larger the organic ion, the more hydrophobic the surface becomes.

The exchange reaction for primary amine ions can be written

$$Na - clay + RNH_3^+ \rightleftharpoons RNH_3 - clay + Na^+$$

Using a series of primary n-alkyl amine ions, Slabaugh (62) found that the equilibrium constant for this reaction increased with the number of carbon atoms in the amine from 0.77 for methylamine ions to 102 for octadecylamine ions. Comparable values were obtained by Cowan and White (16) and Weiss (66). The increase in the equilibrium constant with the number of carbon atoms is probably due to the increased van der Waals forces for the larger ions. In general, it is difficult or impossible to replace large organic cations with smaller ones.

Cowan and White (16) observed incomplete exchange when the amine ion had fewer than eight carbon atoms even in the presence of excess amine ion. They suggested that the platelets did not separate far enough to make all the sites available for exchange. For amines with more than eight carbon atoms, the exchange capacity was exceeded. Chemical analysis of the exchanged clay showed none of the anion originally associated with the amine salt was present, indicating that free amine produced by the hydrolysis reaction

$$RNH_3^+ + H_2O \rightleftharpoons RNH_2 + H_3O^+$$

was being adsorbed. This conclusion was confirmed by Grim, Allaway and Cuthbert (25) who reported a decrease in pH in the exchange reaction of amines with twelve or more carbon atoms but no pH change with eight carbon atoms.

The primary n-alkylammonium clays were first studied systematically by Jordan (35) who determined the c-spacing as a function of the chain length and found a stepwise separation of the platelets by increments of 4Å, which is about the van der Waals thickness of a methyl group. He concluded that the zig-zag carbon chains were oriented parallel to the clay surface. With dodecylamine ions there was no longer sufficient surface area to accomodate the longer carbon chains and two layers formed. This conclusion was substantiated by calculations using the known surface area available per exchange site.

Rex and Bauer (60) observed the same c-spacings as Jordan for primary n-alkylammonium montmorillonites prepared in acetone solutions of 1 meq amine ion/g clay. However if more amine ion was added, 4-12 meq/g, they observed spacings corresponding to a platelet separation equal to the length of the amine, and concluded the ions were oriented vertical to the platelet surface.

Weiss (66) found that when an excess of the free amine or the corresponding primary alcohol was adsorbed on a primary n-alkylammonium montmorillonite, the c-spacing indicated two layers of vertical ions. He proposed that the adsorbed amine or alcohol molecules were also oriented vertical to the clay surface and parallel to the amine ions.

Several other studies have been made of adsorption on primary n-alkylammonium montmorillonites. Taking advantage of the hydrophobic nature of the clays, Cowan and White (14, 15) were able to selectively adsorb phenol from dilute aqueous solutions. They found the maximum phenol adsorption with the dodecylammonium clay, and increase or decrease in the number of carbon atoms in the amine ion reduced adsorption. Carter (12, p. 25-35) observed the same phenomenon with methanol vapor and water vapor adsorption. Cowan and White postulated that the interlaminar adsorption involved both van der Waals bonds between the nonpolar portion of the adsorbate molecule and the carbon chain of the amine ion, and hydrogen bonding of the hydroxyl group to the exposed clay surface; and that the maximum adsorption occurred when organophilic and hydrophilic surfaces were present in approximately equal amounts.

Steric considerations are also involved, especially in the case of water adsorption. The separation of the platelets in the dry clay doubles between the decylammonium clay and the dodecylammonium clay as the carbon chains begin to overlap, thus making more space available for adsorption between the platelets before further separation is necessary.

Neither of these studies considered changes in c-spacing during the adsorption process. Expansion would necessarily affect the amount of adsorption, and simultaneous measurement of adsorption and expansion could help clarify the mechanisms involved in the adsorption process. Barrer and Kelsey (3) adsorbed various organic vapors on dimethyldioctadecylammonium bentonite simultaneously measuring the c-spacing of the clay. Adsorption of saturated hydrocarbons such as n-heptane, iso-octane and cyclohexane did not expand the platelets; however benzene, pyridine, toluene and dioxane, compounds which are aromatic and/or contain polar groups, caused an expansion of about 12Å. This would indicate that the van der Waals forces involved in the adsorption of saturated hydrocarbons on amine carbon chains are not sufficient to expand the clay platelets without an additional interaction between the adsorbate and the surface of the clay.

Houser (29) discovered that certain organo-montmorillonites form gels when dispersed in organic liquids. Jordan (36, 37, 38), using a series of primary n-alkylammonium montmorillonites, has studied this phenomenon in detail. He found that gelation was slight in liquids of a nonpolar nature and that in general the gel volume increased with increasing dielectric constant of the liquid. The most effective liquids were those which combined highly polar with nonpolar characteristics, for example nitrobenzene. However, gelation could occur in nonpolar hydrocarbons if small amounts of a highly polar organic liquid were added, for example 3% ethanol in n-heptane. He concluded that two factors were involved in the gelation process: 1) high adsorption energy of a polar group on the uncovered portion of the platelet surface thus forcing the platelets apart and making the amine cations more accessible, and 2) high solvation energy of the bulk liquid for the amine chains. Both these conditions are fulfilled by a single liquid like nitrobenzene or by a binary system like ethanol-heptane.

Van Olphen (64, 65) has attempted to explain gelation phenomena in terms of the electric double layer; and Granquist and McAtee (21) adapted his approach to the behavior of organo-clays. When methanol, for example, is added to a hydrocarbon suspension of the clay, the molecules are first adsorbed in a single oriented layer on the surface of the clay. The organic cations are displaced away from the surface but remain associated with it. Addition of more methanol increases the dielectric constant of the bulk liquid and the organic cations become solvated. The optimum gel strength occurs when the cations are solvated but still remain associated with the methanol-covered surface. Platelets are then mobile but edge-to-face contacts are possible giving the gel its structure. Further solvation causes dissociation of the cations from the platelets which increases the repulsion between platelets and they separate completely.

Theories of Adsorption

Adsorption can be thought of as the distribution of a species between a vapor (or liquid) phase and the surface of a solid phase. The amount of vapor adsorbed on the solid surface is a function of both temperature and pressure, and increases with increasing pressure and decreasing temperature. It is most convenient experimentally to obtain the isotherm, that is, to measure the amount adsorbed at various pressures and at a constant temperature. The temperature dependence can then be found from a family of isotherms.

Adsorption is generally divided into two large classes, chemisorption and physical adsorption. Chemisorption is distinguished by some degree of chemical interaction between the adsorbate and the surface of the adsorbent. Consequently the energies of adsorption may be quite large and similar to those of chemical bond formation. Chemisorption is important in contact catalysis and has been studied primarily in that context. Physical adsorption occurs as a result of nonspecific attractive forces such as van der Waals forces between the adsorbate and the adsorbent, and can be thought of as the condensation of the gas on the solid surface. The energy of adsorption is exothermic and comparable to that of liquification of the adsorbate. Chemisorption and physical adsorption are usually distinguished by the amount of heat evolved in the adsorption process. In some cases, however, both processes may be involved and no clear distinction is possible.

Adsorption on clay surfaces, although often involving specific coulombic interactions such as hydrogen bonding, shows properties characteristic of physical adsorption. Slabaugh and Kennedy (63), Carter (12, p. 30-36) and Barrer and Kelsey (2, 3) have observed that the isosteric heat of adsorption of both polar and nonpolar vapors on alkylammonium montmorillonites approaches the heat of liquification as the coverage approaches the monolayer calculated from the BET equation. In addition, the adsorbate can be recovered from the clay surface chemically unchanged by lowering the pressure, as is characteristic of physical adsorption.

Ideally adsorption-desorption isotherms should coincide. Often they do not, and the resulting phenomenon is called hysteresis. Various explanations have been suggested. Zsigmondy (67) suggested it was due to capillary condensation. Pores in the surface are filled by multilayer adsorption but are desorbed by evaporation from a concave meniscus. Hysteresis is caused by the lower vapor pressure associated with the meniscus. A second explanation was suggested by Hirst (31) who used models to show that hysteresis could be expected with swelling solids where the surfaces were sufficiently close together for surface forces to contribute appreciably to the cohesion of the solid. This could account for the hysteresis observed with clay systems, particularly when expansion of the platelets is involved.

In addition to being the most convenient form for obtaining and plotting experimental data, the adsorption isotherm is also the form from which most theoretical treatments are developed. A very simple and basic equation was developed by Langmuir (40) based on the following assumptions: 1) the energy of adsorption is constant, which implies uniform sites and no interactions between adsorbate molecules, 2) the adsorption is on localized sites, which implies no translational motion of adsorbate molecules in the plane of the surface, and 3) the maximum adsorption possible corresponds to a complete monomolecular layer. The isotherm equation can be derived either from kinetic (40) or statistical (18, p. 828-831) considerations. The result in linear form is

$$P/v = 1/bv_m + P/v_m$$

where P is the pressure, v the amount adsorbed per gram of solid, v_m the amount adsorbed per gram to form a monolayer, and b a constant related to the saturation vapor pressure.

A great many experimental isotherms fit the Langmuir equation reasonably well in cases where only a monolayer is formed, such as in chemisorption and adsorption of large molecules from solution. Physical adsorption of vapors, however, usually involves more than one layer. Brunauer, Emmett and Teller (10) extended the Langmuir approach to multilayer formation. Their basic assumption was that the Langmuir equation applied to each layer, with the added condition that the energy of adsorption for the first layer have some special value while for all succeeding layers it equal the heat of liquification of the adsorbate. The resulting equation, known as the BET equation, can also be derived either by kinetic (10) or statistical (13, 30) considerations to give the result

$$P/(P_o - P)v = 1/cv_m + (P/P_o)(c - 1)/cv_m$$

where P_o is the saturation vapor pressure, c a constant related to the energy of adsorption and P, v and v_m have the same meanings as previously. The plot of $P/(P_o - P)v$ versus P/P_o is known as a BET plot and the constants c and v_m can be found from the slope and intercept. The specific surface area of the adsorbent can be found by multiplying v_m by the actual area of the adsorbate molecule. The BET equation has been applied most successfully to adsorption of relatively inert gases, such as nitrogen, at temperatures below their normal boiling point. Even then the BET plot gives a straight line only between P/P_o values of 0.05 to 0.35.

The success of the BET equation motivated various workers to propose modifications to correct oversimplifications in the assumptions. Brunauer et al. (11) modified the BET equation by considering adsorption in capillaries. Hüttig (34), by assuming that the adsorbed molecules covered by second and higher layers exert a vapor pressure, obtained the equation

$$(P/P_o)\ (1 + P/P_o)/v \ = \ 1/cv_m \ + \ P/P_o v_m$$

Ross (61) found that Hüttig's equation often gave a better fit than the BET equation.

Harkins and Jura (28) developed an equation based on an entirely different model. They assumed that in some region of the isotherm the adsorbate behaves as a condensed film. They proposed a two-dimensional equation of state for the film and obtained the equation

$$\ln P/P_o \ = \ B - A/v^2$$

where B is a constant and A is proportional to the surface area of the adsorbent. Most isotherms that fit the BET equation also fit the HJ equation. However, it is uncertain which model is physically more correct.

The BET equation was first applied to low temperature adsorption of nitrogen on clays by Emmett, Brunauer and Love (17) and Makower, Shaw and Alexander (46). The latter found that the montmorillonite surface areas obtained from the BET plot corresponded to those calculated from the known particle size; and they concluded that nitrogen was adsorbed on the external surfaces and edges but could not penetrate between the platelets.

Water molecules are adsorbed between the clay platelets, and good straight lines from BET plots over the range $P/P_o = 0.05\text{-}0.35$ have encouraged various workers (20, 50, 56) to calculate total surface areas of clays from water vapor adsorption. As discussed earlier, however, Quirk (59) pointed out that the surface areas calculated by this method are not valid since the water molecules are adsorbed between the platelets not in a monolayer but in hydration spheres about the cations. He postulated that a straight line BET plot is obtained only because the fundamental assumption of a constant energy of adsorption of the first layer is fulfilled.

Straight line BET plots have also been observed by Slabaugh and Kennedy (63), Carter (12, p. 25-30) and Barrer and Kelsey (2, 3) for the adsorption of organic vapors on alkylammonium montmorillonites. The surface areas calculated from the v_m values depend not only on the clay but also on the adsorbate used. As yet, there appears to be no satisfactory physical interpretation of these v_m values.

II. EXPERIMENTAL

The clays used for this study were a series of primary n-alkylammonium bentonites. The organo-clays were prepared from ion exchanged, centrifuged, Wyoming bentonite obtained from the Baroid Division, National Lead Co., Houston, Texas. The clay had a cation exchange capacity, CEC of 92 meq/g (62). Solutions of the amine in isopropyl alcohol were titrated with acetic acid and added to a 1% by weight suspension of the sodium clay in water. A 25% excess of the alkylammonium ion, based on a CEC of 100 meq/g, was used to insure complete exchange. After several hours the hydrophobic organo-clay was filtered off, extracted with isopropyl alcohol in a Soxhlet extractor for 48 hours, air dried, and ground to 170 mesh. Eight different organo-clays were prepared and will be designated as follows

4C - n-butylammonium bentonite
6C - n-hexylammonium bentonite
8C - n-octylammonium bentonite
10C - n-decylammonium bentonite
12C - n-dodecylammonium bentonite
14C - n-tetradecylammonium bentonite
16C - n-hexadecylammonium bentonite
18C - n-octadecylammonium bentonite

Chemical analysis of the clays, prepared as described above and dried in vacuo, is given in Table 1. The CEC is exceeded for amines larger than decylamine and, as discussed earlier, is due to adsorption of the free amine on the organo-clay.

Table 1. Chemical analysis of the organo-clays.

Sample	Carbon	Hydrogen	Apparent CEC
4C	4.89%	1.67%	115 meq/g
6C	5.65	1.93	91
8C	7.21	2.32	91
10C	10.57	2.46	106
12C	12.92	3.17	116
14C	16.84	3.61	134
16C	17.87	3.92	129
18C	19.01	3.91	121

The amines used to prepare the clays were the corresponding Armeens produced by Armour Chemical Division and were used without further purification. The adsorbates, methanol, 95% ethanol, 1-propanol, n-heptane, nitromethane and ethylacetate, were purified by distillation of the reagent grade chemicals.

The adsorption isotherms were determined gravimetrically using an adsorption balance of the type originally described by McBain and Bakr (48) and shown schematically in Figure 3.

Attached to the vacuum manifold were reservoirs for adsorbate storage, a mercury manometer and a McLeod gauge, two adsorption columns and a vacuum X-ray camera. The clay samples, contained in buckets of 0.0005 inch tin foil with handles of 0.0056 inch copper beryllium wire, were suspended in the adsorption columns by means of quartz springs and thin glass extension rods. Coded marks were painted on the extension rods. As gas was adsorbed and the weight in the bucket increased, changes in the position of the marks were followed with a cathetometer. The sensitivity of the cathetometer was 0.1 mm, and weight changes as low as 0.1 mg, or 0.4 mg/g clay for a 250 mg sample, could be detected. The mercury manometer was read with an eyepiece and pressures were estimated to 0.2 torr.

The upper portion of the adsorption columns was in a constant temperature air bath and the lower portion, which contained the clay samples, was immersed in a constant temperature water bath. The latter was maintained at $27.0 \pm 0.1^{\circ}C$.

The X-ray equipment used in the experiments was a General Electric Model XRD-5 diffractometer with copper targets and No. 2 SPG detector and strip-chart recorder. The standard sample holder was replaced by a specially designed vacuum X-ray camera shown in detail in Figure 4. X-rays entered and left through sealed Mylar windows. The sample was held in the X-ray beam by clips which

Figure 3. Gravimetric adsorption balance.

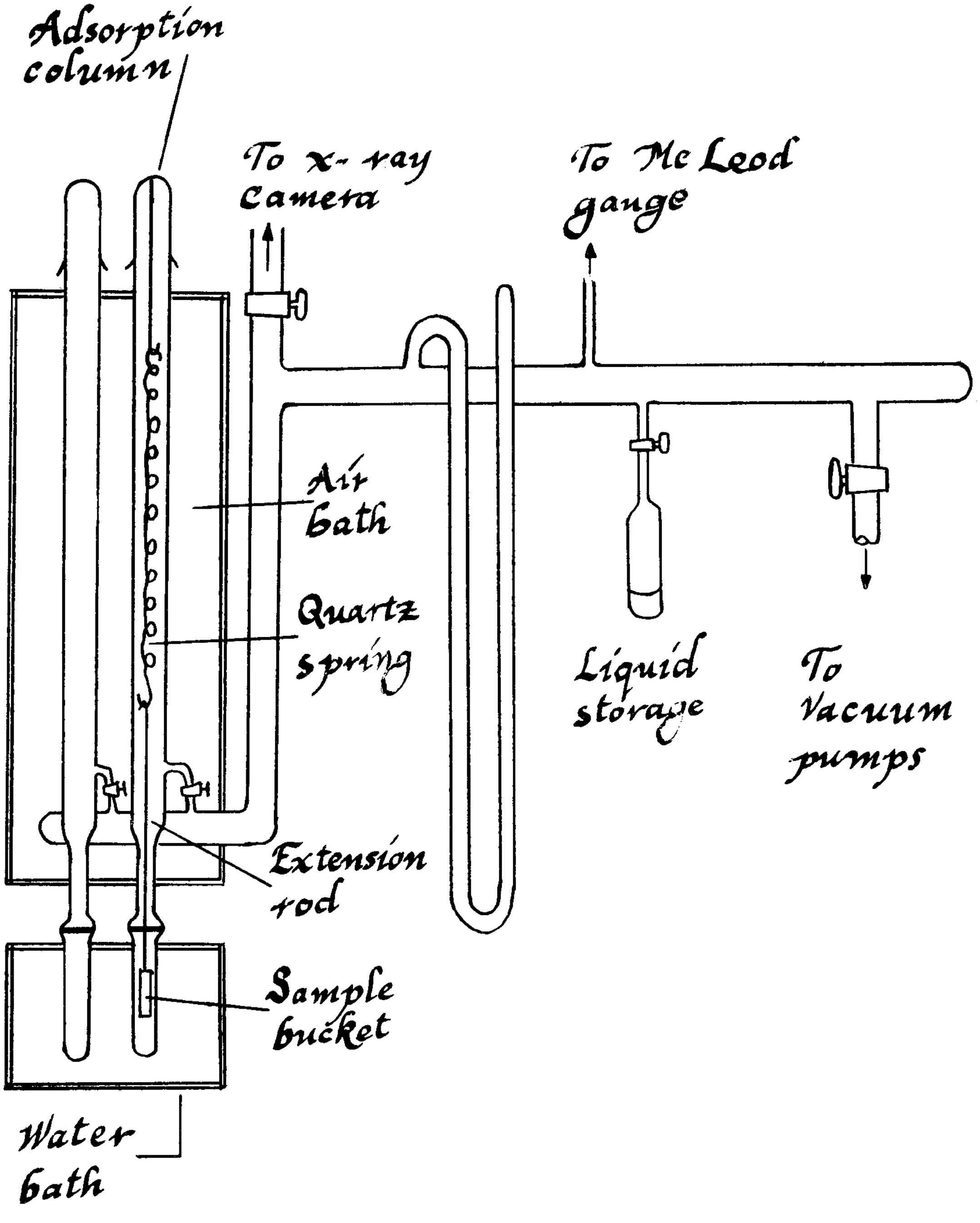
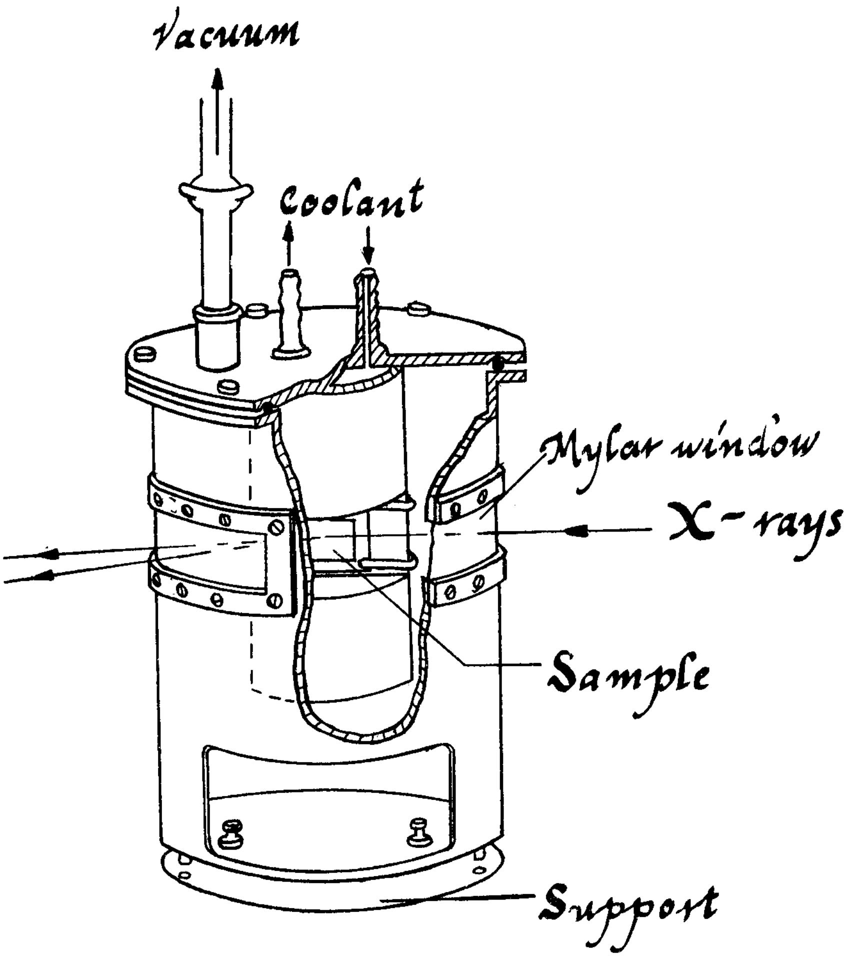


Figure 4. Vacuum x-ray camera



also secured it against an inner chamber through which water circulated. In this way the temperature of the sample was controlled. The cover was sealed on the camera with a rubber o-ring and the whole assembly connected to the vacuum manifold by means of a pair of ball joints. The ball joints also allowed the camera to turn while the diffraction pattern was scanned.

It was desired that the samples for X-ray analysis be oriented so that only reflections from the c-spacing would be observed. A method described by Brindley (8) was used: drops of an ethanol-benzene solution were added to the dry clay forming a paste which was spread on a glass slide and allowed to dry slowly. Diffraction patterns of slides prepared in this way showed only sharp, intense 001 spacings with four or five higher orders and a weak peak at about 27Å due to the Mylar windows.

Before each adsorption isotherm was run, clay samples of about 250 mg were weighed into the foil buckets, suspended from the springs and sealed into the adsorption columns. A slide of the same clay was prepared and sealed into the vacuum camera. The whole system was then carefully outgassed for about 24 hours. The extension of the springs and the X-ray diffraction pattern were recorded before and after outgassing. Usually only the 001 reflection was scanned, but for spacings greater than 25Å both the first and second orders were recorded. Angles were read to 0.1°.

Small increments of the adsorbate were then let into the system. After each addition the system was allowed to reach equilibrium, which took from 30 minutes to 12 hours depending on the adsorbate, and the spring extension and X-ray diffraction pattern recorded. In general, about 30 increments of adsorbate were added until the saturation vapor pressure was reached.

A number of n-heptane isotherms were run in which various amounts of ethanol had been pre-adsorbed on the clay. These isotherms were obtained by allowing the system to reach equilibrium under a known ethanol pressure and then adding small increments of n-heptane. It was assumed that mixtures of the two gases obeyed Raoult's law, and the pressure of n-heptane was taken to be the difference between the observed pressure and the initial ethanol pressure. However the n-heptane pressures that could be obtained were limited by the formation of an n-heptane-ethanol azeotrope, and for this reason some of the isotherms could not be completed.

In order to calculate the c-spacings corresponding to possible orientations of the amine chains, it was necessary to know the thickness of the clay platelet. The distance between the planes of oxygen atoms in the montmorillonite platelet has been accurately determined by Gatineau and Méring (19) to be 6.62Å. If the van der Waals radius of an oxygen atom is 1.40Å (all atomic radii and bond lengths used are those by Pauling (57)), the thickness of the platelet is

6.62 + 2(1.40) = 9.42Å.

The lengths of the alkylammonium ions were calculated from a trans-trans arrangement of the carbon chains. The calculated c-spacing was then taken to be the sum of the length of the alkylammonium ion and the thickness of the platelet. The possibility of hydrogen bonding between the ammonium group and the clay surface, which would decrease the calculated spacings by about 0.2Å, was ignored as the experimental c-spacings were determined to only 0.1° or about 0.4Å.

When the observed c-spacing was significantly less than that calculated, the angle of inclination of the amine chains to the platelet surface, α, was calculated by the relationship

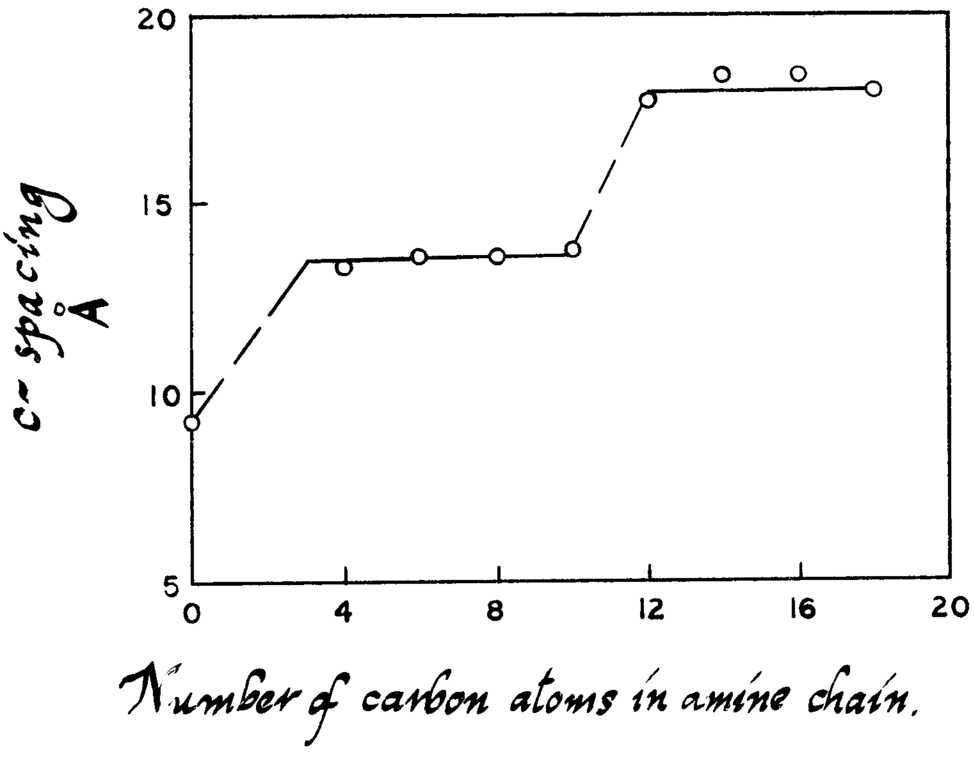
$$\sin \alpha = (\text{observed spacing} - 9.4)/(\text{calculated length of ion})$$

III. RESULTS AND DISCUSSION

The observed c-spacings of the dry clays are shown in Figure 5 and agree with those found by Jordan (36). Two plateaus are observed separated by about 4Å, which is about the van der Waals thickness of a methyl group. Therefore, the first plateau corresponds to a single layer of amine chains between the clay platelets with the chains oriented in a prone position. Beginning with the 12C clay there is no longer sufficient surface area available to accommodate the amine chains in a single layer. Consequently two layers are formed corresponding to the second plateau. Jordan also calculated the surface coverage of the clays and found that for the 12C clay only 57% of the platelet surface was covered by the amine chains. This increased to 79% for the 18C clay.

The experimental isotherms were all inverted S-shaped curves typical of multilayer physical adsorption. They were reproducable within the experimental error and showed the expected hysteresis (Figure 6). The isotherms did not give linear HJ plots, but the BET plots were linear in the range $P/P_o = 0.10 - 0.35$ (Figure 10). Consequently the BET plots were used to calculate v_m values, $v_m = (\text{slope} + \text{intercept})^{-1}$, for all the isotherms. The v_m values for water and methanol adsorption agreed with those calculated by Carter (12, p. 30).

Figure 5. c-Spacing of alkylammonium bentonites.



Water, methanol and ethanol isotherms for the 12C, 14C, 16C and 18C clays are shown in Figures 7, 8 and 9, along with the corresponding c-spacings. In all cases, the 12C clay showed the greatest adsorption, and as the length of the amine chain increased, the amount of adsorption decreased. This trend is reflected by the v_m values shown in Table 2, and is at least partly due to the lower surface coverage by the amine chains in the case of the 12C clay, that is, there is more surface area available for adsorption between the layers without displacing the amine chains and forcing the platelets further apart.

Table 2. v_m values for water, methanol and ethanol adsorption.

Sample	Water	Methanol	Ethanol
12C	16.4 mg/g	35.4 mg/g	50.8 mg/g
14C	-	29.0	-
16C	11.0	28.8	35.7
18C	10.6	28.7	34.0

With water adsorption there is no change in the c-spacing even at high P/P_o values. With methanol and ethanol adsorption there is no significant change until fairly high P/P_o values where the spacing rapidly increases and then levels off again as P/P_o approaches 1.0. This change occurs between $P/P_o = 0.8 - 0.9$ for methanol adsorption and at somewhat lower P/P_o values for ethanol adsorption. Table

3 shows that the final c-spacings correspond to those calculated for a vertical orientation of the amine chains between the platelets. That is, the alkylammonium ions are now in an extended, upright position resembling pillars holding the platelets apart. The sudden opening of the platelets makes available for adsorption the surface area formerly occupied by the amine chains. This might be reflected by the isotherms in a step or sudden increase in slope as adsorbate molecules are adsorbed on this new surface. However this is observed only in the case of ethanol adsorption on the 18C clay, and to a lesser extent with methanol on the same clay, where a vertical step is observed immediately following the increase in c-spacing.

Table 3. c-Spacings for methanol and ethanol adsorption.

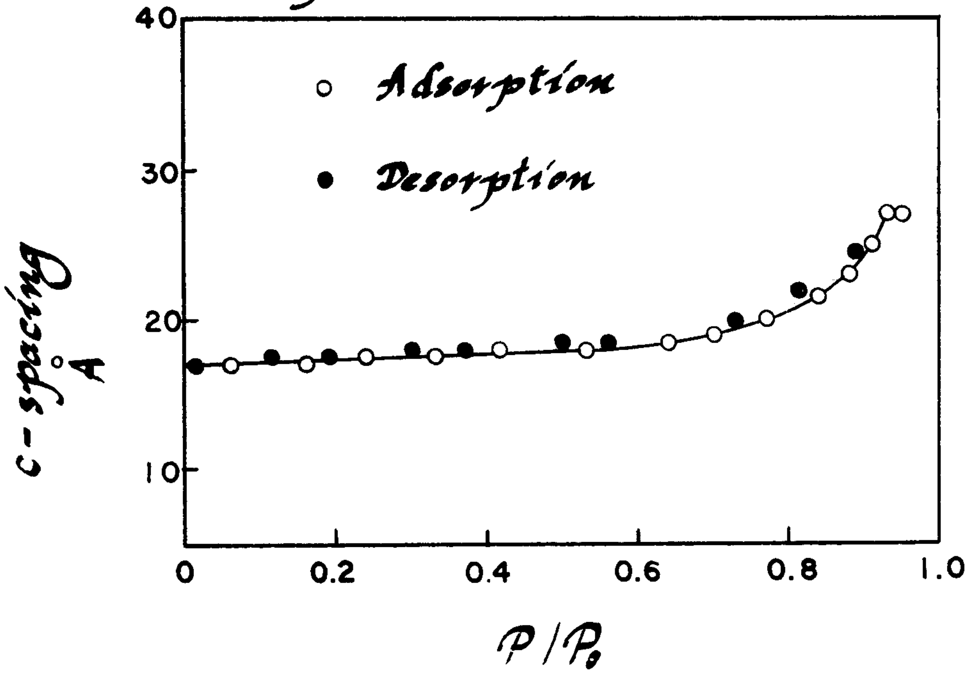
Sample	Dry	Methanol	Ethanol	Calculated
12C	17.7A	26.8A	26.8A	26.7A
14C	18.4	29.4	-	29.2
16C	18.4	31.5	31.5	31.7
18C	18.0	34.0	34.0	34.2

Brown and MacEwan (9) and MacEwan, Amil and Brown (45) have calculated the diffraction patterns that would be expected from clays with random interstratification of two different c-spacings. They found that a peak associated with one spacing migrates to a near-by peak associated with the other spacing as the relative proportions of the two spacings change. The peak position generally follows an S-shaped curve. If the separation (in Å^{-1}) between the extreme positions is small, the movement is almost linear. As the separation increases, the S becomes more marked and the peak becomes less intense and broader than at the extreme positions. If a peak of one component is located between two of the other, the peak first broadens and then separates into two. In the middle region of the S, the peak becomes very diffuse and if the middle region is nearly vertical may almost disappear. It should be emphasized that at intermediate positions the spacing corresponding to the observed peak has no physical significance.

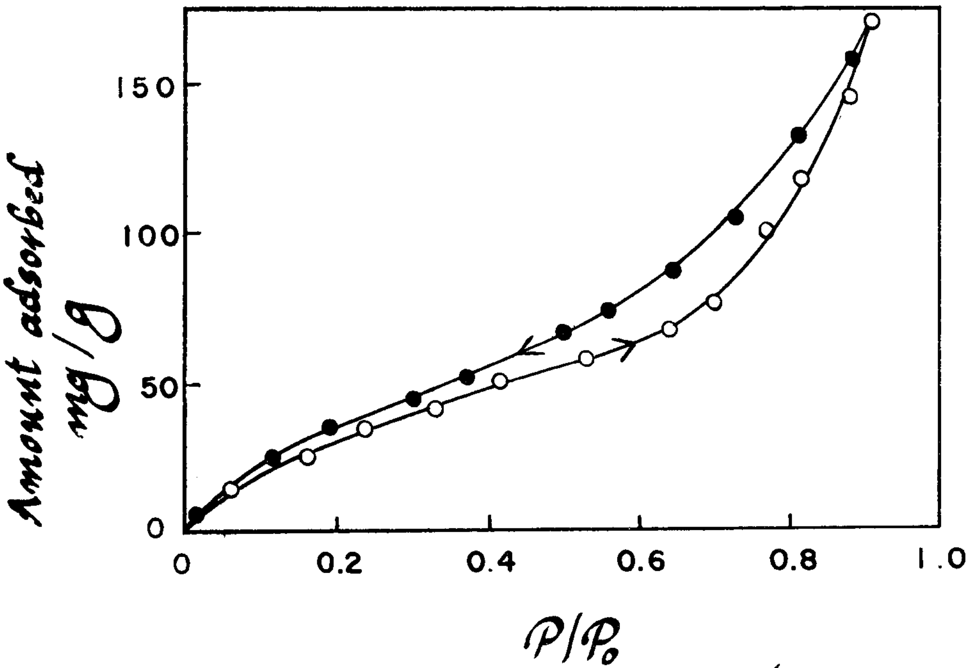
This approach satisfactorily explains the changes in the diffraction pattern observed during adsorption. Two examples are given in Figure 11. With adsorption of ethanol on the 12C clay, the peak migrated from 18.8Å to 26.8Å in an S-shaped manner. With the adsorption of ethanol on the 18C clay, however, the 002 spacing was close enough to the more intense 001 spacing so that the original peak first broadened, almost disappeared, and then separated into two peaks. Therefore, during the adsorption process the only spacings present were those corresponding to the dry clay and the fully expanded clay, so it would seem that the platelets did not open up gradually but rather popped open all the way.

The effect of changing the number of carbon atoms in the

Figure 6. Adsorption and desorption of methanol on dodecylammonium bentonite at 27 °C.

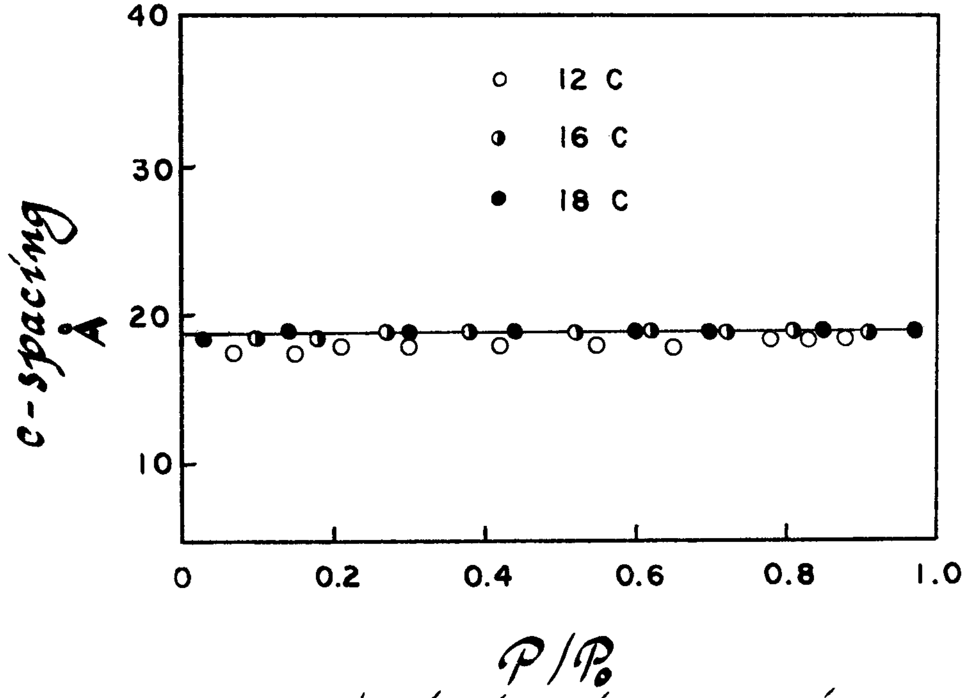


Variation in c-spacing

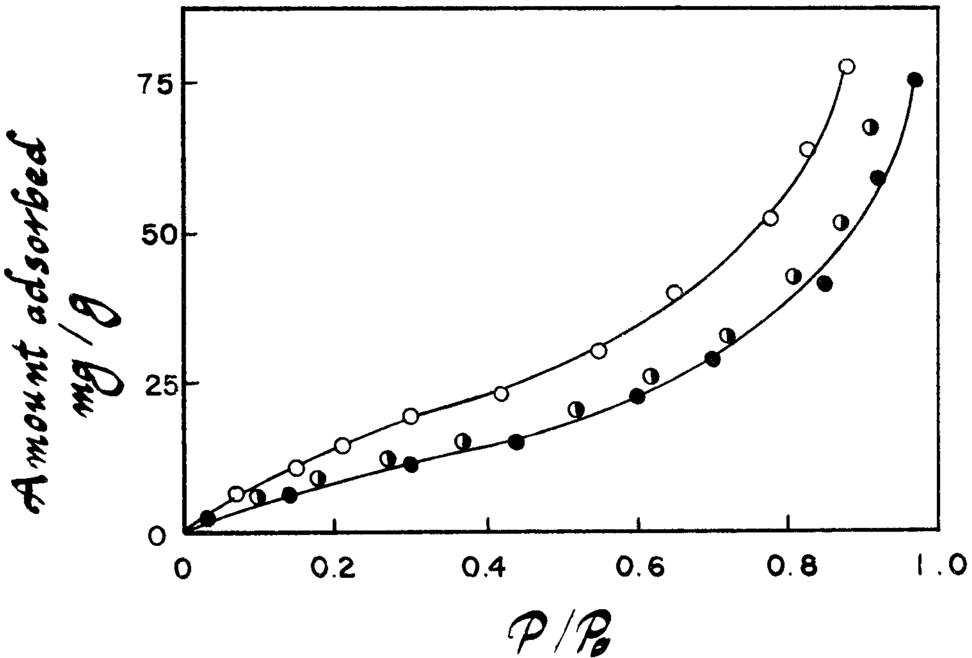


Adsorption and desorption isotherms

Figure 7. Water adsorption on alkylammonium bentonites at 27 °C.

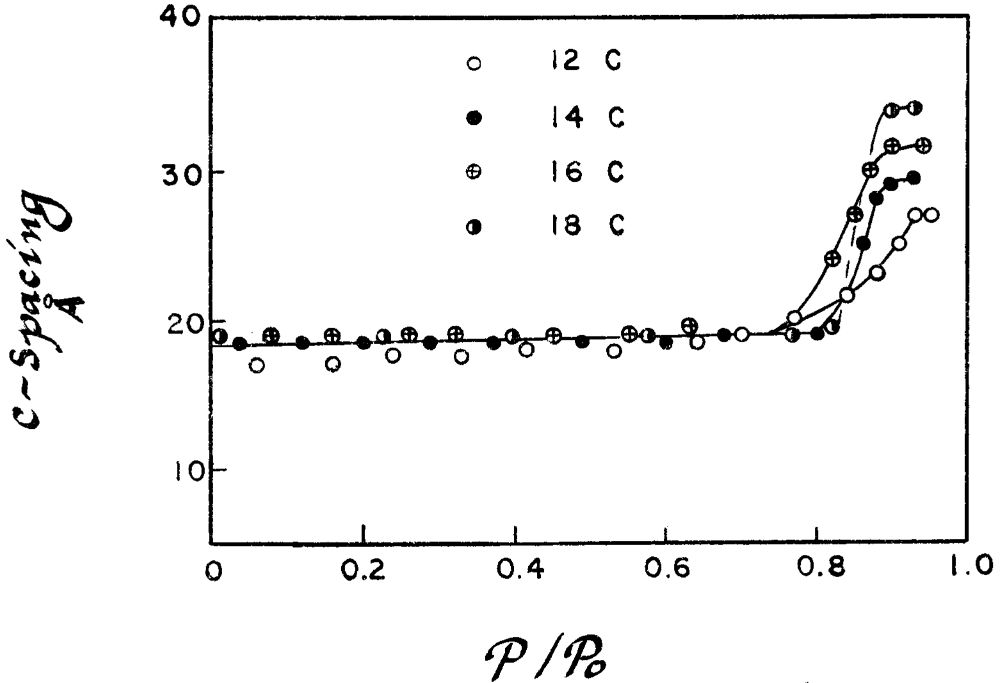


Variation in c-spacing

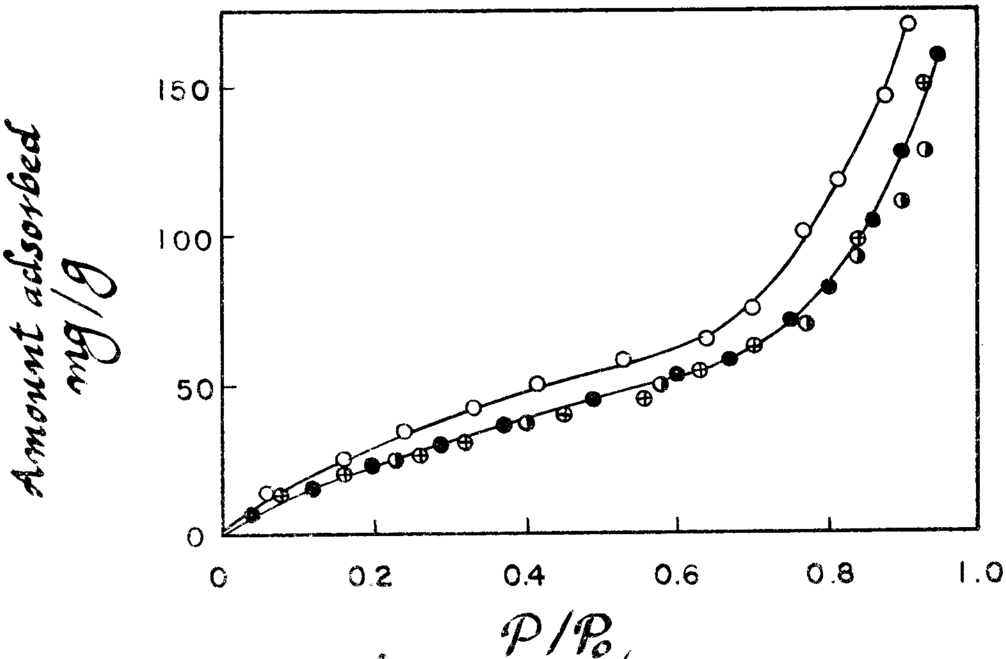


Adsorption isotherms

Figure 8. Methanol adsorption on alkylammonium bentonites at 27 °C

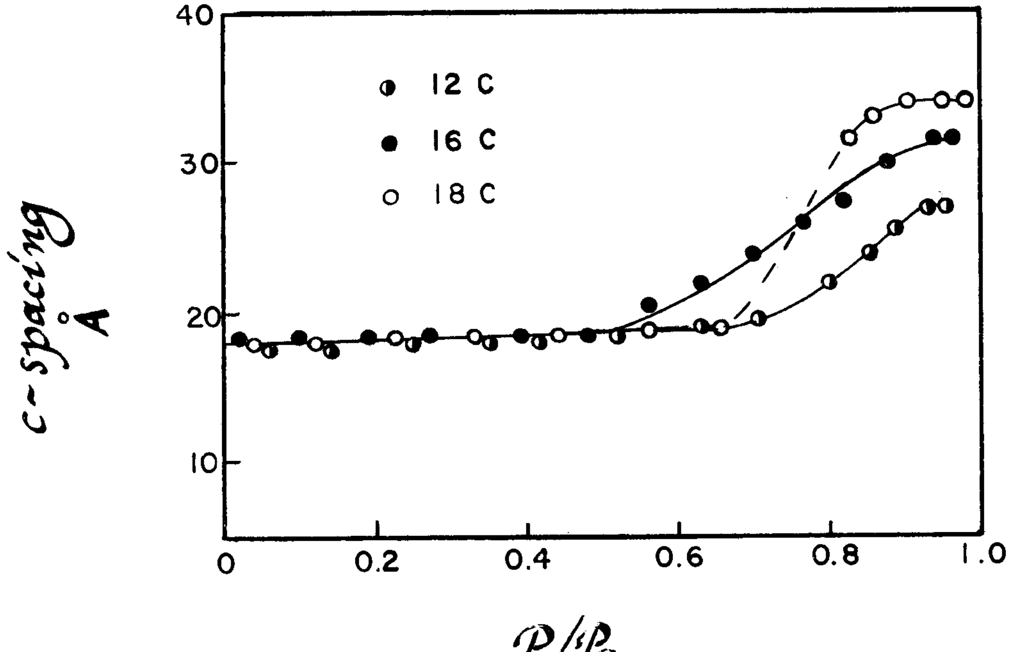


Variation in c-spacing

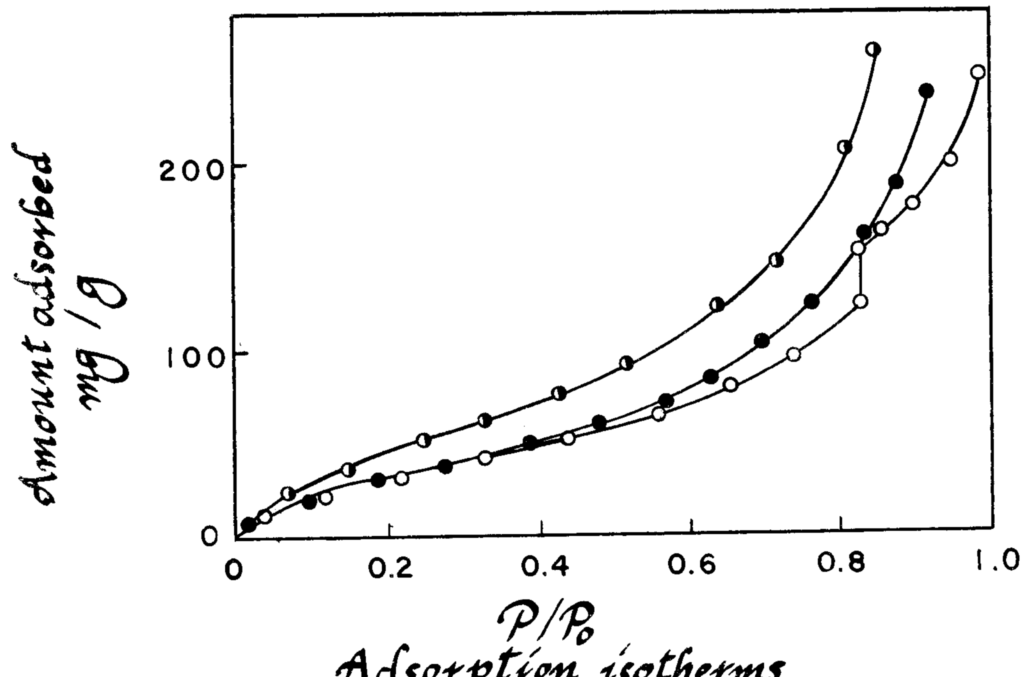


Adsorption isotherms

Figure 9. Ethanol adsorption on alkylammonium bentonites at 27 °C



Variation in c-spacing



Adsorption isotherms

Figure 10. BET plots for ethanol adsorption at 27 °C.

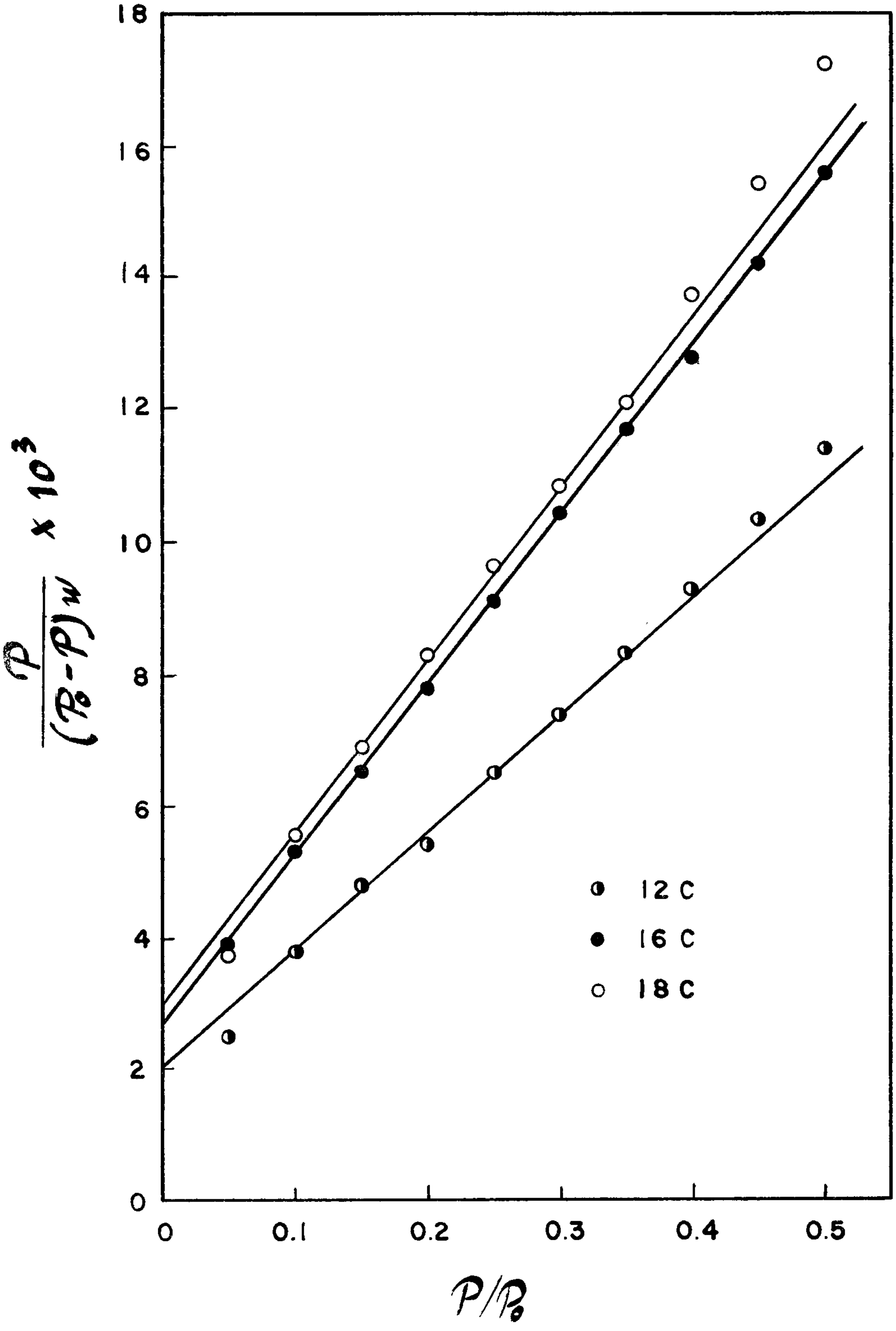
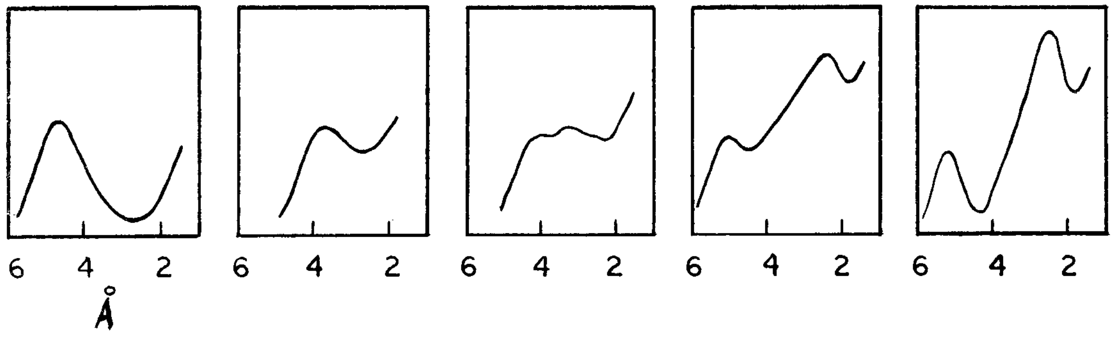


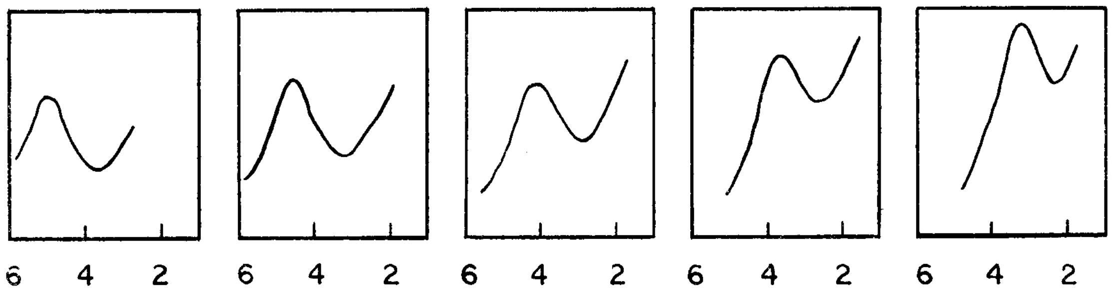
Figure 11. Typical x-ray diffraction patterns. (abcissa is an arbitrary logarithmic intensity scale.)

Beam slit 1°
Detector slit 0.05°
Scan speed 2°/min



$P/P_0=0$ $P/P_0=0.66$ $P/P_0=0.74$ $P/P_0=0.83$ $P/P_0=0.99$

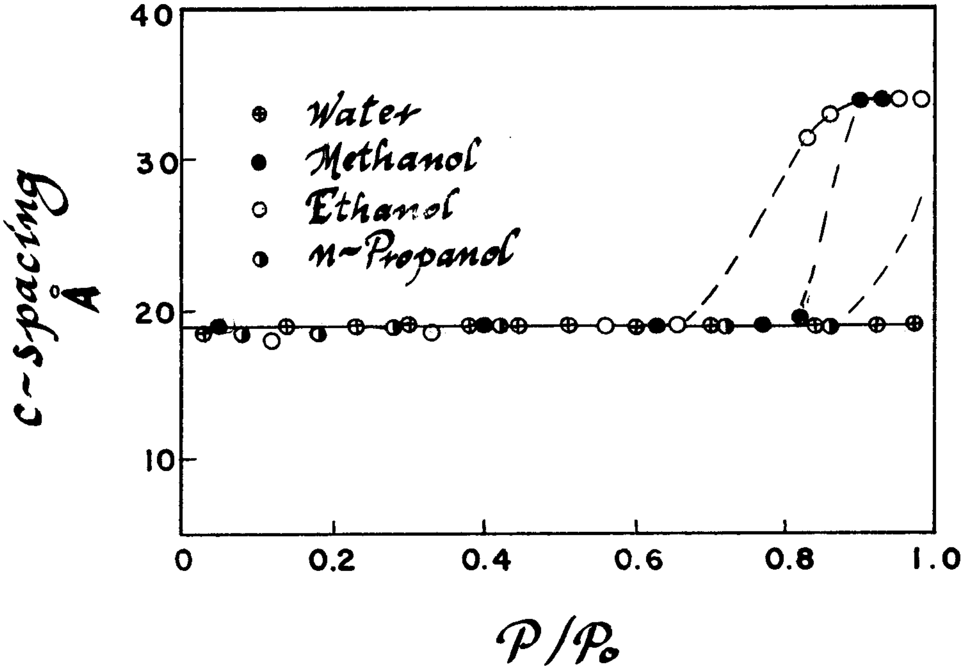
Ethanol on 18 C



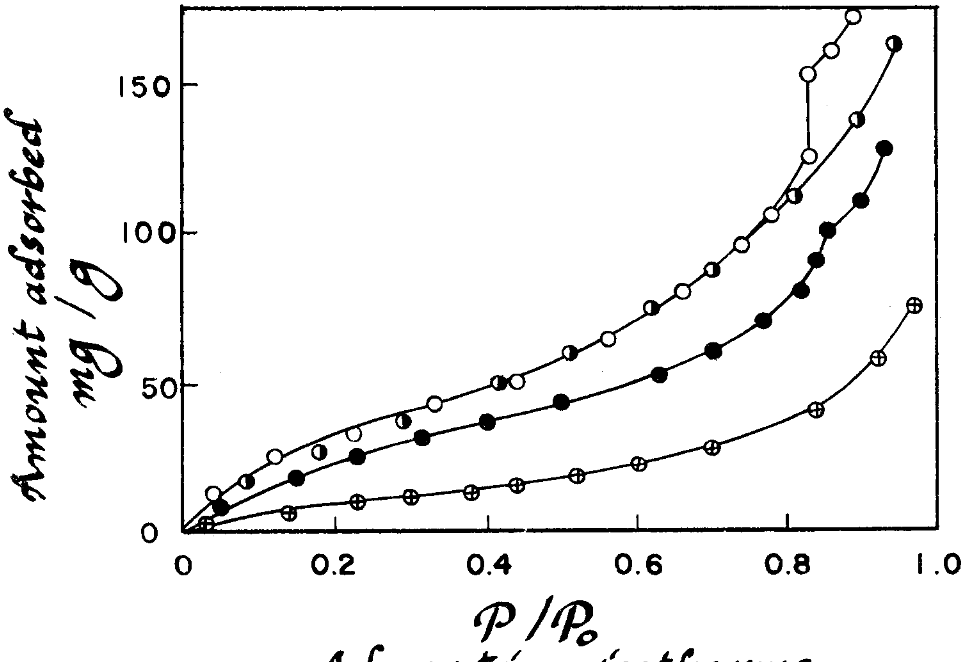
$P/P_0=0$ $P/P_0=0.63$ $P/P_0=0.73$ $P/P_0=0.86$ $P/P_0=0.95$

Ethanol on 12 C

Figure 12. Adsorption of various alcohols on octadecylammonium bentonite at 27 °C.



Variation in c-spacing



Adsorption isotherms

alcohol adsorbate is shown in Figure 12 which gives the isotherms and c-spacings for the adsorption of water, methanol, ethanol and 1-propanol on the 18C clay. The amount of adsorption increased with increasing number of carbon atoms up to ethanol but fell off again with propanol. This trend is reflected by the v_m values given in Table 4, and also parallels the gel volumes measured by Jordan (36) for the 18C clay in the liquid alcohols, also given in Table 4.

Table 4. c-Spacings and v_m values for octadecylammonium bentonite.

Adsorbate	c-Spacing	α	v_m	gel volume*
Water	18.0A	-	10.6 mg/g	2ml
Methanol	34.0	-	28.7	12
Ethanol	34.0	-	34.0	18
1-Propanol	34.0	-	32.8	16
n-Heptane	18.0	-	1.5	-
Ethylacetate	32.0	65.5°	69	-
Nitromethane	26.0	42.0°	77	-

*gel volume of a two gram sample, from Jordan (36).

As discussed previously, the adsorption of water did not affect the c-spacing of the clay, while methanol and ethanol adsorption caused a rearrangement of the amine chains resulting in an upright orientation. This same rearrangement occurred with adsorption of 1-propanol. However, the peaks in the diffraction pattern were broad and not as intense as those observed with methanol and ethanol, indicating that all the platelets had not expanded.

No change in c-spacing was observed with the adsorption of either water, a highly polar substance, or n-heptane (Figure 13), a highly nonpolar substance. However adsorption of molecules which possess both polar and nonpolar characteristics, such as methanol and ethanol, resulted in a rearrangement of the amine chains from a prone to a vertical orientation. Consequently, any explanation of this behavior must involve both the polar and nonpolar nature of the adsorbate.

It is possible to explain the results if the adsorption is assumed to take place in two steps. First of all, adsorbate molecules are adsorbed on the outer surfaces of the clay and on the exposed interior surface, that is, on the surface of the platelets not covered by amine chains. In the case of alcohols, adsorption on the oxygen surface of the platelet probably involves some hydrogen bond formation. As discussed, this type of adsorption would account for the greater adsorption by the 12C clay. The slight increase in c-spacing at low P/P_o values, for example from 18.0Å to 19.0Å for the 18C clay, also indicates that there is some adsorption between the platelets before they begin to open up completely. So far, the amine chains have not been displaced, but retain their original orientation.

The second step occurs at higher pressures and involves the rearrangement of the amine chains which assume an upright orientation. Adsorption accompanying this rearrangement is of two forms. The polar portion of the adsorbate molecule is adsorbed on the surface vacated by the amine chains, and the nonpolar part is adsorbed on the alkylammonium ions filling the space between the upright chains. Or in other words, the energy necessary to separate the platelets is supplied by two exothermic adsorption processes, adsorption of a polar group on the platelet surface and attraction of a nonpolar group for the amine chains.

The absence of any change in c-spacing with water adsorption can now be explained. The highly polar water molecules are easily adsorbed on the available clay surface. However, the water molecules are too polar to be adsorbed on the amine chains, and adsorption on the platelet surface is not sufficient to separate the platelets. Conversely, n-heptane is adsorbed by the amine chains but not the platelet surface.

Jordan (36) has shown that ethanol, when added to n-heptane in small amounts, is an excellent gelling agent for organo-clays. Since gellation involves separation of the platelets, it has been proposed (21) that the ethanol is first adsorbed between the platelets initiating the separation.

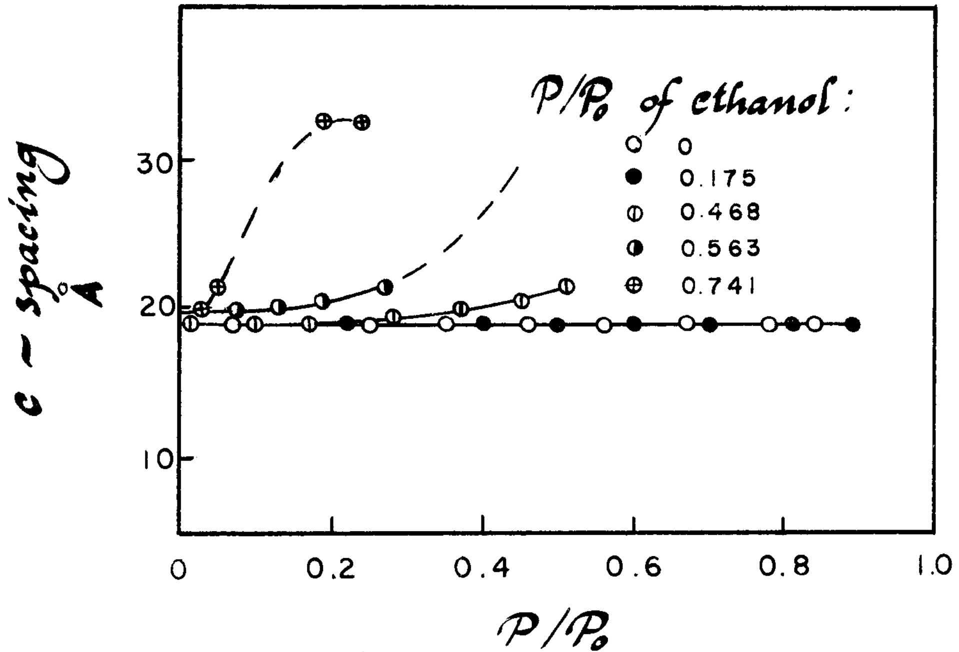
Isotherms of n-heptane adsorption on the 18C clay with various amounts of ethanol pre-adsorbed are shown in Figure 13. The ethanol had no appreciable effect on the n-heptane adsorption until ethanol pressures above $P/P_o = 0.2$. Then the n-heptane adsorption increased as the amount of preadsorbed ethanol increased.

In addition, with ethanol pressures above $P/P_o = 0.2$, the adsorption of n-heptane caused the c-spacing to increase, although the peaks in the diffraction pattern were broad and fairly weak indicating that all the platelets had not expanded. It would seem, therefore, that instead of a single adsorbate supplying both polar and nonpolar groups, separation of the platelets can be effected by use of two adsorbates, one polar and one nonpolar. In this case the ethanol was adsorbed on the platelet surface and the n-heptane on the amine chains.

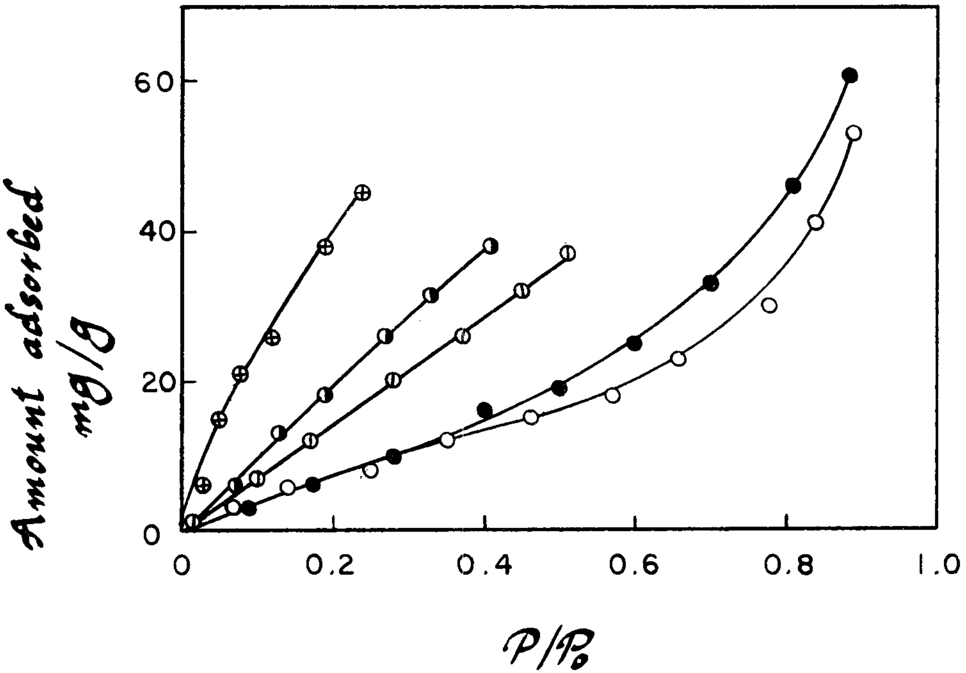
It would have been of interest to examine n-heptane adsorption at an ethanol pressure above $P/P_o = 0.83$. This was impossible, however, due to the formation of an n-heptane-ethanol azeotrope.

Isotherms and c-spacings for two other adsorbates, nitromethane and ethylacetate, on the 18C clay are shown in Figure 14. The amount of adsorption for both adsorbates was much greater than for the alcohols. In both cases, however, the final c-spacing observed was less than that calculated for a vertical orientation of the amine chains. Nevertheless, the diffraction patterns showed sharp, intense peaks indicating a high degree of order in the systems.

Figure 13. n-Heptane adsorption on octadecylammonium bentonite at 27°C with ethanol pre-adsorbed.

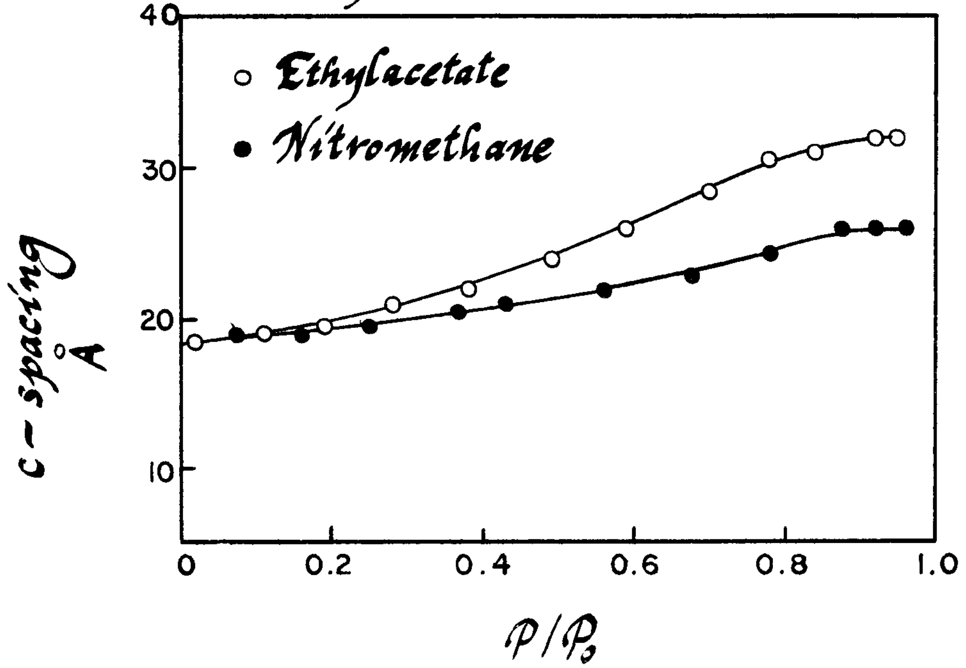


Variation in c-spacing

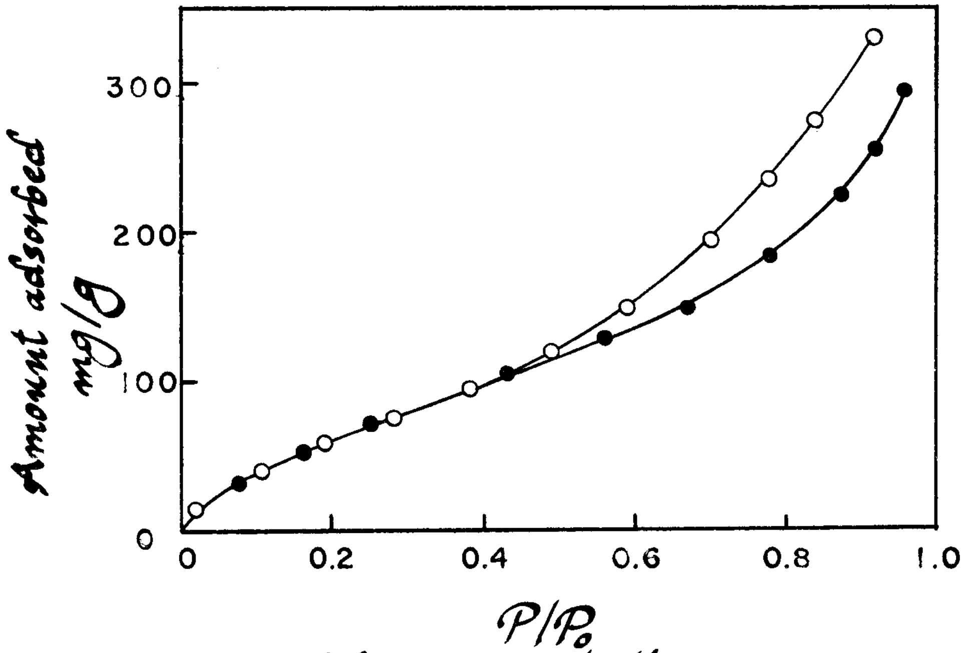


Adsorption isotherms

Figure 14. Nitromethane and ethylacetate adsorption on octadecylammonium bentonite at 27 °C.



Variation in c-spacing



Adsorption isotherms

In the case of ethylacetate, the calculated angle of inclination of the amine chains, 65.5°, is the same as that observed with liquid phase adsorption of n-primary alkylamines on montmorillonite (1, 66). This particular angle of inclination is favored because all three hydrogen atoms of the ammonium group are in a position to form hydrogen bonds with the oxygen atoms of the clay surface.

An analogous explanation in the case of nitromethane is not entirely satisfactory, primarily because there appears to be no particular advantage, such as hydrogen bonding, to be gained by a 42° angle of inclination to account for the high degree of ordering.

However an alternative explanation for the observed spacing is possible. The nitromethane molecules, being quite polar would be strongly adsorbed on the clay surface. However the clay surface is not level, but instead is a hexagonal network of oxygen atoms. The holes in the hexagons are exactly the size of an oxygen atom. Consequently an adsorbed nitromethane molecule could have one of the oxygen atoms of the nitro group sunk into the platelet surface. The part of the molecule above the surface would have essentially the thickness of a methyl group, or 4Å.

Therefore, the adsorption of nitromethane might take place as follows. The very polar adsorbate molecules are adsorbed on the platelet surface, and partially sunk into it. The adsorbate is too polar to be adsorbed on the amine chains as is necessary if they are to assume a vertical orientation. However the van der Waals attraction between the amine chains and the methyl group of the adsorbate is sufficient to displace the amine chains from the surface permitting two complete layers of nitromethane molecules, one on each surface, to be adsorbed. The spacing would then increase by twice the diameter of a methyl group, or 8Å, which is exactly the increase observed.

The mechanism proposed above predicts that the final c-spacing is independent of the length of the amine chain. This could be easily tested by adsorbing nitromethane on a different clay. It might also be of value to examine the adsorption of nitroethane.

IV. SUMMARY AND SUGGESTIONS FOR FURTHER WORK

Surfaces of the stacked platelets comprise 90% of the surface area of clay minerals. Consequently, X-ray measurement of the platelet separation presents an ideal tool for studying adsorption phenomena. For this purpose vacuum apparatus had been constructed to include both gravimetric adsorption balances and an X-ray camera in order that the diffraction pattern could be scanned under the same conditions that the adsorption was measured.

In this way adsorption of a variety of compounds on a series of primary n-alkylammonium bentonites was studied. X-ray spacings of the dry clays indicated that the amine ions were oriented with the zig-zag chains parallel to the platelet surface. No change in this orientation was observed with adsorption of very polar or nonpolar substances. However organic compounds with polar functional groups were adsorbed with an increase in c-spacing. It was postulated that the adsorption process leading to the expansion involved both adsorption of the polar group on the oxygen surface of the clay and van der Waals bonding between the nonpolar portion of the adsorbate molecule and the amine chain. This resulted in a rearrangement of the amine chains and their removal from the platelet surface to give an increase in the c-spacing. However the final c-spacing, and therefore the final orientation of the amine chains, appeared to depend on the nature of the polar functional group. Qualitative explanations were made for the various proposed orientations.

Several suggestions for further work relating to this study can be made.

1) Many other adsorbates whose behavior might also be of interest should be investigated, for example ketones, nitriles, ethers, halogenated compounds, aromatic compounds, and series of compounds with the same functional group analogous to the series of alcohols used in this study.

2) Jordan (36) found that the organophilic properties of primary n-alkylammonium bentonites with amine chains of less than 12 carbon atoms were negligible. Therefore adsorption of polar adsorbates such as water and nitromethane might give quite different results with these clays.

3) The net energy of interaction in the expansion process involves several terms. The energy necessary to separate the platelets and remove the amine chains from the platelet surface must be supplied by the polar and nonpolar adsorption processes. No attempt was made in this study to either measure or calculate any of the energies involved. It would certainly be of value to attempt such a calculation.

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