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Addition of aliphatic amines to montmorillonite to improve its adsorption capacity for organic pollutants in aqueous solution

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ADDITION OF ALIPHATIC AMINES TO MONTMORILLONITE TO IMPROVE ITS ADSORPTION CAPACITY FOR ORGANIC POLLUTANTS IN AQUEOUS SOLUTION

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Addition of aliphatic amines to montmorillonite to improve its adsorption capacity for organic pollutants in aqueous solution

by

Timothy Allen Wolfe

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
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ABSTRACT

Adsorption is one of the prominent separation techniques used in the treatment of wastewaters containing soluble organics. Activated carbon has been employed almost exclusively in adsorbing the 129 "priority pollutants", as defined by the Environmental Protection Agency (EPA), from water and wastewater. Synthetic resins have recently begun to receive attention, but are derived from energy related sources, as is activated carbon. A few clays have been considered for use as adsorbents, but in nearly all cases the clays were used in their natural state. This research has explored the addition of the chloride salts of propylamine, dodecylamine, and dodecyldiamine to sodium montmorillonite (a smectite) in an attempt to improve its adsorptive capacity for removing organics from water and wastewater. X-ray diffraction analysis, differential thermal and thermogravimetric analyses, infrared spectroscopy, and scanning electron microscopy, were used to determine the interaction between montmorillonite and the alkylammonium salts. Replacement of exchangeable cations on the interlamellar surface of montmorillonite with alkylammonium ions has been shown by several researchers to permit ready intercalation of a wide variety of polar and nonpolar organic species. Adsorption isotherms conducted with acetaldehyde, acetone, benzene, butanol, chloroform, dimethylphthalate, hexanol, nitrobenzene, octanol, phenol, and toluene as the solutes showed some indication of intercalation of these eleven organic compounds. Intercalation of these compounds at low organic solution concentrations, 100 and 1,000 milligrams per liter, was found within the scope of the present study by x-ray diffraction and gas chromatography techniques not to be sufficient to make the alkylammonium-montmorillonites or the untreated montmorillonite totally competitive with current adsorbents used in the water and wastewater field. Adsorption of the eleven organic pollutants by the clays generally ranged from 10 to 50 percent of the amounts expected to be adsorbed on activated carbon at similar solute concentrations. Intercalation noted at high organic solution concentrations, up to 100 percent, was more significant and suggests the clays would be efficient in removing these organics at higher concentrations. X-ray diffraction results obtained make it possible to predict the orientation of the three alkylammonium ions and the eleven organic compounds in the interlamellar space of the montmorillonites.

INTRODUCTION

Regulations concerned with water quality can be divided into five general categories: Physical parameters, microbiological parameters, radioactive materials, inorganic chemicals, and organic chemicals. The discovery of potentially carcinogenic organic compounds in the New Orleans' drinking water supply in 1974 brought increased attention to the organic chemical contaminants. Studies in November, 1974, at the Environmental Protection Agency (EPA) research laboratories in Cincinnati, Ohio identified 154 organic compounds in drinking water supplies of communities on the Ohio, Potomac, and Mississippi Rivers (Appendix A (1)).

Programs were undertaken to identify the major contributors of the organic compounds to public drinking water sources. Industrial and municipal discharges, accidental spills, runoff from agricultural and urban areas, and from the chlorination process at water treatment plants were investigated. Of the 154 compounds, 113 were classified as major products or by-products of chemical manufacturers according to the Stanford Research Institute's 1973 Directory of Chemical Producers, U.S.A. No longer was it only important to remove or to prevent the formation of trihalomethanes in water treatment, but it also became necessary to monitor more closely materials being discharged into raw water sources.

On February 2, 1977, the EPA proposed a rule establishing mechanisms and procedures for enforcing national pretreatment standards controlling the introduction of nondomestic wastes into publicly owned treatment works (POTW s). While all nondomestic discharges of waste to POTWs were covered by the regulations, there were at least 87,000 existing industrial dischargers to POTWs in 21 industrial categories.

A June 7, 1976, Consent Decree in the case of the Natural Resources Defense Council, Inc., versus Train as the representative of EPA required EPA to review 65 toxic pollutants (Appendix A (50, 75)), both organic and inorganic, which may be discharged by the 21 industrial categories, and to establish pretreatment standards for any of the 65 toxic pollutants and any other nontoxic pollutants found not to be susceptible to treatment by POTWs or which would interfere with the operation of the POTW.

Over 700 organic compounds have been identified in drinking waters across the United States, but the focus of categorical pretreatment standards has been on the 65 toxic pollutants selected on the basis of a review of available data on 232 pollutants of greatest environmental concern at the time the Consent Decree was developed. This list of 65 toxic pollutants has more recently been expanded in a new EPA list of 129 "priority pollutants" (Appendix A (75)).

The massive volume of literature on priority pollutants in water and wastewater outlines a need for their removal. There are numerous separation techniques used to remove organics from water and wastewater. Adsorption is one of the techniques most commonly used to accomplish this separation, and a major section of the proposed regulations actually required the application of granular activated carbon treatment for contaminated drinking water supplies (68).

It is interesting to note that, with adsorption occupying such a large portion of the work on the removal of organics from water and wastewater, activated carbon is the adsorbent used almost exclusively. Synthetic resins are beginning to receive some attention but they too are derived from an energy related source. Naturally occurring clays have received relatively little consideration as adsorbents for removing unwanted organics from water and wastewater. This would seem to be unusual since clays have been shown to remove humic compounds from water, and it is known that humic substances compose a significant portion of the organics in secondary effluents from biological wastewater treatment processes (84, 110). Nearly all adsorption studies that have been performed with clays have used the clay in its natural state, with no attempt to improve the clay's adsorptive capacity by pretreatment with various chemicals.

The major effort of this research was to treat naturally occurring montmorillonite with the salts of aliphatic amines of varying chain lengths in an attempt to improve its adsorptive capacity for undesirable organics found in water and wastewater.

APPLICATIONS OF ORGANO-CLAY COMPLEXES

Organo-clay complexes have been utilized for many years for (27, 95) lubricants, coating for paper, cosmetics, medicinals, gellants in paints, color bodies removal in lube oil refining, catalyst activation and deactivation phenomena, soil conditioning, insulation and sealants in buildings, stationary phases in gas chromatography, structural hydraulic fluids in shock absorbers, ablatants in nose-cones, viscosity control in polyester resins, reinforcing fillers in elastomers, oil base drilling fluid modifiers, dye receptors in fibers, carbonless typing paper, better additives in paper making, etc. The ceramic industry is a big user of clay technology largely because of the contribution clays have in improving the molding and drying properties of the wares produced.

Ariizumi and Iwai (3) developed a new method for accelerating the strength development of concrete by utilizing halloysite, a hydrated kaolinite structure, treated with lime and sulfate as an admixture for Portland cement. Novak and Gregor (96) found that the maximum decolorizing capacity of acid-treated montmorillonites corresponds to treatments that provide maximum surface area. The active clay material in soil, particularly in combination with small amounts of organic matter, exerts a tremendous influence on soil properties. Clays have been shown to affect the physical properties of soil which are of importance to the growth of plants (102). Soil engineers have used quaternary ammonium chlorides to stabilize soils for several years.

It is interesting to note that with all the knowledge available concerning the adsorptive capacity of clays, little use has been made in the field of water and wastewater treatment, of the increased adsorptive capacity generated when organic materials are added to the clays.

MONTMORILLONITE STRUCTURE

Bentonite is the rock name used to describe a drab and cream-colored bedded clay. It is essentially volcanic ash in which the glass has been hydrated and which has lost most of its constituents except silica and alumina. Bentonite contains two classes of materials (66). The first class consists of sand and silt as impurities, and includes grains that range from 0.005 to 1.0 mm in diameter. These impurities are largely plagioclase, orthoclase, and biotite, with accessory quartz, glass, apatite, zircon, and agate. The second class of materials is clay as the predominant component, and includes all grains less than 0.005 mm in diameter. This class is montmorillonite containing water, silica, and alumina.

Montmorillonite, the clay fraction, can be separated from the raw bentonite by sedimentation or centrifugation techniques. Montmorillonite is one mineral of the smectite, or montmorillonoid group of minerals. It is an expanding, three-layer clay structure (an octahedral sheet sandwiched between two tetrahedral sheets) derived from that of the prototype pyrophyllite by substitution of other atomic species for central atoms of the polyhedra. A schematic for a typical unit cell of montmorillonite is shown in Figure 1 (129). Figure 2 shows a model of the montmorillonite lattice structure. The hexagonal holes in the tetrahedral layers are evident in this model.

In the tetrahedral sheet, tetravalent Si is sometimes partially replaced by trivalent Al ions. In the octahedral sheet, there may be

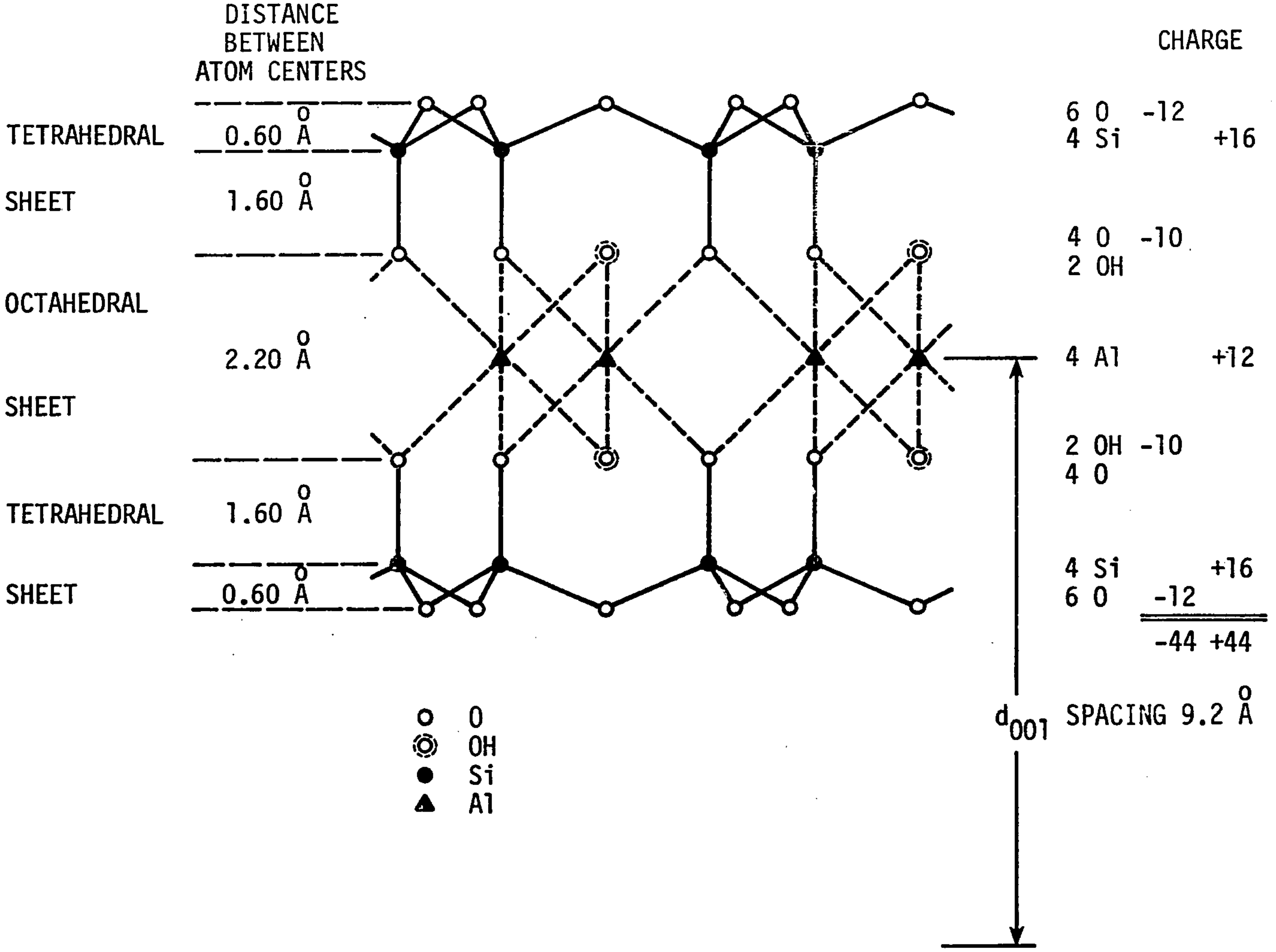


Fig. 1. Schematic of a unit cell of montmorillonite (129)

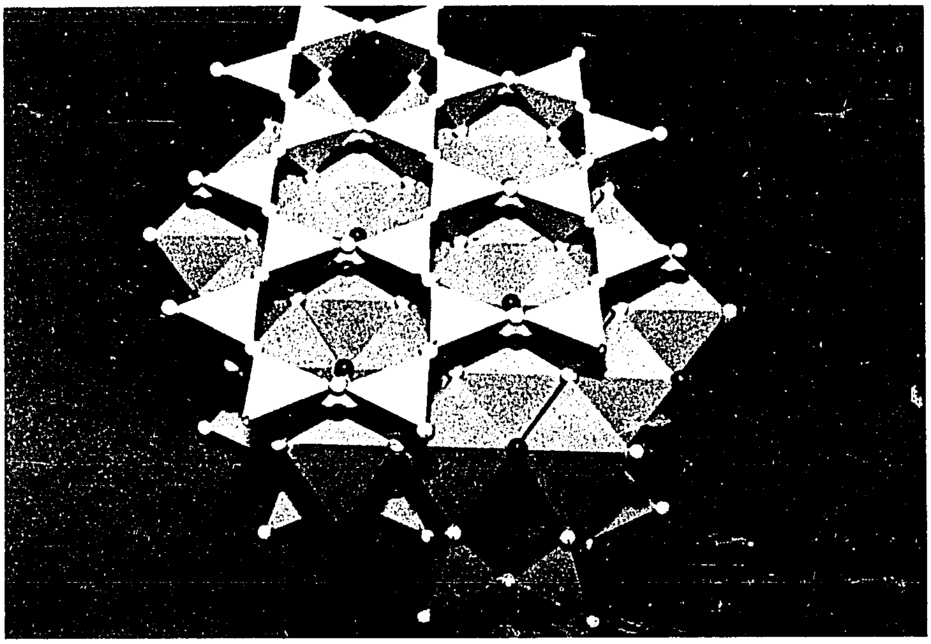


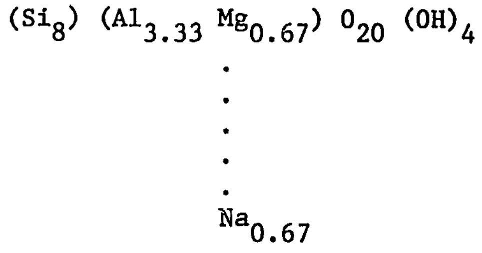
Fig. 2. Model of montmorillonite lattice

replacement of trivalent Al by divalent Fe, Mg, etc. This replacement of one ion for another is referred to as isomorphous substitution. Substitution of an ion by one with a lower positive valence results in an excess of negative charge which is compensated for by the adsorption of cations too large to be accommodated in the interior of the lattice, usually Ca or Na ions. These compensating cations are referred to as exchangeable cations because they can easily be exchanged for other cations, either inorganic or organic, in the presence of water.

Stacks of unit layers held together by van der Waals forces form a montmorillonite particle. Exchangeable cations are located on each side of each unit layer in the stack; hence, they are present between the unit layers as well as on the external surfaces. Their presence between the layers causes a slight increase in the basal spacing of montmorillonite compared with that of pyrophyllite, the prototype mineral.

A considerable amount of work has been done to determine the chemical composition of montmorillonite. A few representative chemical analyses are shown in Table 1 (23, 41, 94). Several additional chemical analyses can be found in van Olphen and Fripiat's handbook (130).

If the cation-exchange capacity (CEC) and the chemical composition of the clay are known from chemical analysis, it is possible to assign the substituting ions to either the tetrahedral or octahedral sheets. The formula for a unit cell of a typical montmorillonite in the sodium form with a CEC of 91.5 milliequivalents per 100 grams of clay would be:



$$(Si_8)\ (Al_{3.33}\ Mg_{0.67})\ O_{20}\ (OH)_4 \cdots Na_{0.67} \qquad (1)$$

Another important concept in the description of the montmorillonite system is the types of surface areas. In this study, "basal plane surface" refers to areas on tetrahedral layers in the montmorillonite structure. The "basal plane surfaces" can be divided into two categories. The exposed exterior tetrahedral layers laying on either side of a montmorillonite particle are termed "exposed basal plane surfaces." The interior basal plane surfaces between unit layers are referred to as "interlamellar surfaces." The exposed exterior areas on the broken-edges, along the sides of the montmorillonite particles, are termed "broken-edge surfaces."

X-ray diffraction analysis plays an important role in the identification of clays and the determination of interactions between clay lattices and organic species adsorbed between the clay layers. The unit layer of montmorillonite, consisting of an octahedral sheet sandwiched between two tetrahedral sheets, serves as a unit plane in x-ray diffraction and defines the unit crystal (unit cell) of the clay. The unit cell is a parallelepiped representing chemical composition and the geometry of a crystalline compound. Directions of the three sides of the parallelepiped form the crystallographic axes a, b, and c. The unit plane of the clay is the base of the parallelepiped. The intercepts of all other planes with the crystallographic axes may be

Table 1. Chemical composition of several montmorillonites

Fraction	Weight (Percent)(23)	Weight (Percent)(41)	Weight (Percent)(94)
SiO_2	61.3	61.47	49.21
Al_2O_3	22.4	22.17	22.61
Fe_2O_3	3.55	4.32	0.43
FeO	0.39	-	-
TiO_2	0.11	0.09	nil
CaO	n.d.	0.14	1.95
MgO	2.81	2.73	2.13
Na_2O	2.71	3.18	0.45
K_2O	0.044	0.03	trace
P_2O_5	-	0.02	-
H_2O	5.82	6.02	23.71[a]
	99.13	100.17	100.49

[a] H_2O content reported in the reference corresponds to total H_2O. The author states that numbers of hydroxyl groups present is uncertain, therefore, recommends leaving out the water percentage in computation of unit cell formulas.

expressed by the unit distances (vectors) a_o, b_o, and c_o. Intercepts of the unit layers of montmorillonite with the c axis are of importance to this study as the unit layers of montmorillonite are visualized as being stacked on top of each other parallel to the plane defined by the a and b axes.

The Bragg equation for diffraction is:

$$n\lambda = 2\ d\ \sin\theta \tag{2}$$

where

n = the order of reflection

λ = wavelength of x-rays ($\lambda = 1.541$ Å for copper K_α radiation)

d = distance between identical planes in the c direction

θ = angle at which reflection occurs.

By including the n in the Miller symbol of the reflection indices and rearranging, this equation can be written in the form:

$$\sin\theta_{(hkl)} = \frac{\lambda}{2d_{(hkl)}} \tag{3}$$

where

h, k, and l = Miller indices, integers with a common devisor that are the reciprocal of the intercepts of a given plane with the a, b, and c axes.

For example, if the unit layer of montmorillonite intercepts the a, b, and c axes at ∞, ∞, and 1, the Miller indices would be 0, 0, and 1 and the $d_{(hkl)}$ spacing defined is the d_{001} spacing. If the intercepts of the a, b, and c axes occurred at ∞, ∞, and 1/2, the Miller indices become 0, 0, and 2 and the $d_{(hkl)}$ spacing defined is the d_{002} spacing. The d_{002} spacing would be one-half of the d_{001} spacing. The intensities of these two diffraction peaks depends upon the structure of the montmorillonite and can be affected by expansion of the montmorillonite with water, organic molecules, or other materials.

DISCUSSION OF LITERATURE

The literature review is divided into three sections to permit specific discussions, each centering around an area pertinent to the research conducted in this study. The first section outlines general interactions that are believed to occur between clays and various organic groups. The nature of clays as adsorbents is discussed in this section. The second section deals specifically with the adsorption of amines on montmorillonite and a few other clays. The third section emphasizes adsorption of several organic species on alkylammonium-montmorillonites, montmorillonite treated with the salts of amines before interaction with these additional organic compounds.

General Interactions Between Montmorillonite and Various Organic Groups

It has been recognized for many years that clays have the ability to adsorb many types of organic materials. Experiments performed as long ago as 1845 (128) showed the greater apparent power of clay, over other cultivated soils, to retain the salt of ammonia. At the time it was thought the ability of clay to adsorb ammonia was due to a salt of lime in the soil, and not the free or caustic clay itself (132).

Bonding mechanisms in clay-organic complexes are a long way from being fully understood, even today. The types of bonding mechanisms range from simple mechanical entanglement to the formation of multiple chemical bonds. There is disagreement as to how many such mechanisms exist and which mechanisms apply to each classification of interaction between clays and organic compounds.

The following is a listing of several possible bonding mechanisms that may occur between clay and organic materials (91):

I. Cationic

1. Ion exchange - Organic cations are adsorbed at clay mineral surfaces by ion exchange with cations; neutralizing the negative electrical charges responsible for the cation-exchange capacity of the mineral (E.g. alkylammonium ions adsorbed on Na^+- and Ca^{+2}-montmorillonite, pyridinium adsorbed on montmorillonite, and butylammonium ions adsorbed on vermiculite).
2. Protonation of organic molecules at clay surfaces - Certain organic compounds can become cationic through protonation after adsorption at the clay surface (E.g. NH_3 adsorbed on Na^+- and Ca^{+2}-montmorillonite, urea and various amides adsorbed on H^+-, Al^{+3}-, or Fe^{+3}-montmorillonite, pyridine on Mg^{+2}-montmorillonite, and 3- aminotriazole adsorbed on NH_4^+-montmorillonite).
3. Hemisalt formation - Hemisalt formation occurs when the amount of base adsorbed on a clay exceeds the number of protons available for cation formation (E.g. ethylammonium ions adsorbed on ethylamine-montmorillonite, urea on montmorillonite, and various amides-montmorillonite complexes).

II. Anionic - Although anions are not expected to form complexes with negatively charged clay surfaces, the benzoate anion of benzoic acid has been observed to interact with montmorillonite under certain conditions.

III. Ion-Dipole and Coordination - Interactions between polar, but nonionic, organic molecules and clay minerals has classically been considered one of hydrogen bonding. Extensive work performed on alcohols has shown direct coordination of these organics to the exchangeable cation of the clay surface through their oxygen atoms (E.g. alcohols, ketones, nitrobenzene, and amines interacting with various clays).

IV. Hydrogen Bonding

1. Water bridge - A water bridge is formed when a polar organic molecule links to an exchangeable metal cation through a water molecule in the primary hydration shell (E.g. ketones and nitrobenzene interacting with montmorillonite and acetone adsorbed on Na^+- and Mg^{+2}-montmorillonite).
2. Organic, organic hydrogen bonding - When the exchangeable cation on the clay is an organic cation, the possibility exists of interaction with another species of organic compound through hydrogen bonding (E.g. pyridinium-montmorillonite complexed with ethyl N, N-di-n-propylthiol carbamate and trimethyl-ammonium-montmorillonite interacting with dialkyl amides).

3. Clay mineral oxygens and hydroxyls - Interaction can occur with molecules capable of hydrogen bonding with the oxygens or hydroxyls of clay mineral surfaces (E. g. NH groups of alkylammonium ions complexing with oxygen of the silicate sheets in vermiculite). In most cases, the hydrogen bonds formed with the oxygens and hydroxyls on the surface are weaker than intermolecular hydrogen bonds.

V. van der Waals Forces - These forces are short range, relatively weak physical forces operating between all atoms, ions, or molecules resulting from attraction between oscillating dipoles in adjacent atoms (E. g. long-chain alkylammonium ions adsorbed on various minerals).

VI. Pi Bonding - Unique d orbitals in Cu(II)-montmorillonite allow certain types of unsaturated hydrocarbons to be bound through donation of their pi electrons (E. g.benzene, xylene, toluene, and chlorobenzene complexed with Cu (II)-montmorillonite).

VII. Entropy Effects - Adsorption of some organic polymers from solution on clay minerals is apparently favored if there is a positive entropy change in the system (E. g. glycine polymer adsorbed on montmorillonite).

VIII. Covalent Bonding - Preliminary results suggest it is possible in the geologic column, under relatively high pressures and temperatures and over geologic time, that some covalent bonding between organic matter and silicates may occur (E. g. methyl lithium reacting with water of hydration or structural hydroxyl groups on kaolinite surfaces).

Interactions Between Montmorillonite and Various Organic Groups

Smith (116) was one of the first to investigate extensively the adsorption of organic cations on clay. He concluded that the reaction between bentonite and the salts of several organic bases was one of base-exchange.

Hendricks (64) studied several aromatic amines, diaminofluorene salts, and some aliphatic and heterocyclic salts adsorbed on montmorillonite. His work showed the organic cations to be held to the surface of the silicate layers, not only by Coulombic forces between ions, but also by van der Waals attraction of the molecules to the surface. Hendricks also noted large organic ions to be held more firmly by the clay than are inorganic positive ions, even including hydrogen ions.

Protein and amino acid interactions

A tremendous amount of work has been devoted to adsorption of proteins by montmorillonitic clays. The amounts of protein adsorbed are large (up to 2.4 grams per gram of montmorillonite) and are limited only by the amount of surface available, and not by the sites on the surface of the clay (90). Ensminger and Gieseking (44) prepared albumen-montmorillonite and gelatin-montmorillonite complexes and found the organic materials to be adsorbed in the interlamellar space of the clay. They also discovered adsorption was enhanced in suspensions of low pH and that the adsorption was partly due to the cationic groups in the protein molecule.

Further work by Ensminger and Gieseking (45) centered around the treatment of montmorillonite with varying quantities of hemoblobin, casein, protamine, pepsin, and pancreatin. The data once again showed the proteins to be adsorbed in the interlamellar space. Proteins reduced the base-exchange capacity of the clay when the complexes were acidified, indicating that an increase in hydrogen-ion concentration increased the basic properties of proteins, permitting them to be adsorbed as cations.

Ensminger and Gieseking (46) also investigated the rate of enzymatic hydrolysis of proteinaceous material adsorbed on bentonite that was predominantly montmorillonite. Proteolytic enzymes, rather than microorganisms, were used because microorganisms hydrolyze proteins by producing enzymes, and the hydrolyzing power of enzymes is affected to a lesser degree by environmental conditions than the microorganisms are. The adsorption of albumen and hemoglobin by the bentonite was found to interfere with the enzymatic hydrolysis of these proteins in both acid pepsin and alkaline pancreatin suspensions. This work led Ensminger and Gieseking to postulate that the interference was either due to adsorption of the enzyme by the clay, or that the protein molecule may be oriented in such a way in the interlamellar space of the clay that active groups of the protein were rendered inaccessible to the enzyme.

Talibudeen (123) found that one or two layers of protein could be adsorbed in the interlamellar space of montmorillonite, depending upon the pH and concentration of the suspension. In a gelatin-suspension at pH 2.5 and protein concentrations stronger than one percent, two, 4.3 Å thick monolayers of the polypeptide chains of protein, each strongly adsorbed on the clay mineral sheets, were taken up in the interlamellar space. He was also able to obtain one layer complexes of gelatin with the montmorillonite by using gelatin concentrations of 0.5 percent and less, or by exposing the two layer complexes to a one percent gelatin suspension at pH values greater than 3.5. Talibudeen (125) further noted that proteins, such as virus proteins having a high molecular weight and exhibiting a high degree of crystalline order, could not be incorporated in the interlamellar spaces of montmorillonite.

Pinck (106) showed that monolayers of proteins were more rigidly held to montmorillonite than were polylayers, probably due to van der Waals forces. This idea was reinforced when only twenty percent of the protein in a monolayer complex was shown to undergo decomposition, whereas extensive decomposition occurred in the polylayer complexes.

Amine interactions

Base-exchange is the mechanism by which amines are adsorbed on montmorillonite. Adsorption isotherms obtained are characteristically Langmuir or L-type (53), corresponding to reversible adsorption in which a fixed number of sites on the clay surface participate in the adsorption process. If the number of carbon atoms in the chain does not exceed eight, adsorption has been found not to exceed the cation-exchange capacity of the montmorillonite, but for larger cations adsorption appears to be limited only by the surface area of the clay. With the larger cations, van der Waals interactions dominate the adsorption process and the isotherms become H-type[1] rather than L-type, with the alkyl chains projected in a plane at right angles to the montmorillonite surface.

Bradley (20) studied adsorption of primary and secondary amines with one to six carbon atoms in the alkyl chain and recorded basal spacings between 13.0 and 13.5 Å, indicating that adjacent clay layers were separated by one layer of organic molecules with the zig-zag of the amine chain parallel to the montmorillonite surface. He found from thermodynamic measurements that the affinity of the monovalent organic ion for montmorillonite increased with increasing amine chain length because van der Waals forces and hydrogen bonding were involved as well as the coulombic forces.

Rowland and Weiss (112) investigated four methylamine hydrochlorides, from mono- to tetramethyl, adsorbed on sodium-bentonite. Their work showed two layers of adsorption for the methylamine and dimethylamine in the interlamellar space, with trimethylamine and tetramethylamine forming only a monolayer since the larger cations can fill only one out of every three holes in the oxygen surface of the clay. The base-exchange capacity of the bentonite was found to be satisfied by methylamine when 19.0 percent of the oxygen surface was covered with the molecules standing

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[1] H-type refers to a classification of adsorption isotherms that result when high affinity ions are exchanged with lower affinity ions.

perpendicularly or when 23.5 percent of the oxygen surface was covered with the molecules in a tilted position. The dimethylamine cation was observed to assume two different positions on the oxygen surface. When the plane of the zig-zag amine chain was parallel to the oxygen surface, dimethylamine covered 44.5 percent of the oxygen surface. If the plane of the zig-zag chain was perpendicular to the oxygen surface, 40.0 percent of the surface was covered. The trimethylamine cation is almost disc-shaped, and therefore must lie flat over a hole in the surface of the clay with the cation as close as possible to the negative charge on the oxygen surface. In this position,only one of every three holes can be occupied and 39.0 percent of the bentonite surface was assumed to be covered.

Ammonia interactions

Adsorption of anhydrous ammonia on hydrogen-bentonite was found by Cornet (30) to be highly dependent upon the degree of grinding to which the bentonite had been subjected. When small quantities of ammonia were brought into contact with unground hydrogen bentonite, it appeared to react with exterior basal planes and broken-edge surfaces of the clay. As these reactive surfaces became saturated, the ammonia pressure rose. At about twenty-three mm pressure of mercury the montmorillonite planes were forced apart. The ammonia was adsorbed in the interlamellar space where it reacted with hydrogen ions. Additional adsorption of ammonia was found to follow the customary Freundlich adsorption isotherm pattern.

The adsorption of ammonia on finely ground hydrogen bentonite exhibited an entirely different pattern. As the pressure of the ammonia increased, adsorption increased continuously with no expansion of the clay lattice noticed. Not only did grinding decrease the adsorptive capacity of the clay, but the unground form was capable of retaining 0.81 milliequivalents of ammonia per gram when the ammonia was pumped off at a pressure of 4×10^{-5} mm of mercury; whereas the finely ground form was able to retain only 0.51 milliequivalents per gram of clay.

Mortland et al. (93) found that with montmorillonites expanded with ammonia, the basal spacings decreased in the same order as with the hydration series: $H \simeq Ca > Na \simeq K > Cs$. These findings suggested that the extent to which montmorillonites swell in the presence of ammonia depends on its charge and perhaps on the location of the charge in the octahedral or tetrahedral layer. For H^+- and Ca^{++}-montmorillonites fully expanded by ammonia, the basal spacing was measured at 12.2 ± 0.1 Å. That ammonia was chemisorbed as NH_4^+ ions rather than in the molecular form was confirmed by infrared spectroscopy. Mortland postulated that the ammonia reacted with exchangeable protons in the case of H^+-montmorillonite, and residual water molecules or constitutional OH^- supplied the necessary proton in the base saturated montmorillonites.

Sugar interactions

Greenland (56) studied the adsorption of twenty-seven different sugars on montmorillonites saturated with several different inorganic cations. The amount of adsorption was found to vary with the exchangeable cations in the order: $K < Ca < Mg < H < Na$. Methylated sugars were adsorbed more strongly than were the unsubstituted sugars. Carboxyl- or amino-substituted glucoses were physically adsorbed less strongly than were the unsubstituted sugars. Monosaccharides were less strongly adsorbed than were the disaccharides.

Most of the sugars formed two-layer complexes in the interlamellar space, while some showed only monolayer complexes and others exhibited only two-layer complexes. No adsorption was observed to exceed that represented by the formation of a two-layer complex. Adsorption appeared to commence with solution concentrations of about one percent, and maximum adsorption was observed at a solution concentration of approximately four percent.

Surfactant interactions

Surfactants are classified into two main classes: ionic and nonionic. The ionic class is further subdivided into anionic and cationic groups. Law and Kunze (78) treated Wyoming bentonite with eight surfactants at three treatment rates (100, 50, and 10 millimoles per 100 grams). The surfactants included three anionic, three cationic, and two nonionic compounds.

The anionics were not adsorbed in quantities sufficient to be detected by thermogravimetric measurements and had no effect on basal spacings of the montmorillonite. In contrast to the anionics, adsorption data showed that significant quantities of both cationic and nonionic compounds were adsorbed by the montmorillonitic clays. Large basal spacings were observed at the high and intermediate treatment rates for the cationics and nonionics, reflecting the tendency for large organic molecules to stand on end when crowded between clay plates. In some cases, the data exhibited basal spacings indicative of a tilting of the organic molecules in the interlamellar space.

Herbicide interactions

Interactions between pesticides and soil colloids indicate the fate and behavior of pesticides in soil systems are dependent upon at least seven factors: chemical decomposition, photochemical decomposition, microbial decomposition, volatilization, movement, plant uptake, and adsorption. The phenomenon of adsorption-desorption appears to influence directly or indirectly the magnitude of the effect of the other six factors.

Bailey, et al. (5) reacted H^+- and Na^+-montmorillonites adjusted to pH values of 3.35 and 6.80, respectively, with members of the herbicide families: s-triazines, substituted ureas, phenylcarbamates, aniline, anilides, phenylalkanoic acids, benzoic acids, and picolinic acids. Adsorption isotherms conformed to the Freundlich adsorption equation for nearly all the organic compounds, and none of the groups studied conformed to the Langmuir adsorption equation.

Adsorption occurred to the greatest extent on the highly acidic H^+-montmorillonite compared to the nearly neutral Na^+-montmorillonite. The dissociation constant of the adsorbate was cited as the major factor governing the magnitude of adsorption.

Maximum retention of basic compounds occurs when the surface acidity of clay is at least one to two pH units lower than the lowest dissociation constant of the molecule. An interesting concept was noted when atrazine, an s-triazine with a pK_2 value of 1.68, was adsorbed on the H^+-montmorillonite at pH 3.35. This meant that the pH at the surface of the clay had to be approximately three units lower than the suspension pH, or the atrazine could not have been adsorbed since it would not have been completely associated at pH 3.35.

Alcohol interactions

MacEwan (80) brought air-dried Ca^{++} and NH_4^+ saturated montmorillonite into contact with monohydric and polyhydric alcohol liquids. The monohydric alcohols formed two-layer complexes in the interlamellar space of the montmorillonite for alcohols with one and two carbon atoms in the hydrocarbon chain, and mono-layer complexes with alcohols containing three to ten carbon atoms in the chain. This finding is in agreement with the bonding mechanisms of montmorillonite, since the interlamellar layer consists of two surfaces, each with negative oxygen ions. The shorter chain alcohol molecules are more polar and their positive ends are attracted to the negative ions on each of the two surfaces forming two layers in the interlamellar space. Since the longer chain alcohol molecules are nonpolar, van der Waals forces of attraction are important and the molecules tend to lie flat in the interlamellar space forming only a single layer.

Emerson (43) adsorbed polyvinyl alcohol on montmorillonite forming a two-layer interlamellar complex with the carbon chains perpendicular to the clay surface in which there appeared to be van der Waals contact between the CH_2 groups and the oxygen atoms on the clay surface. This assumption is contradictive of the findings by MacEwan (80).

Brindley and Ray (25) formed complexes between Ca^{++}-montmorillonite and even numbered straight chain primary alcohols containing from two to eighteen carbon atoms. Single-layer complexes were formed for all the alcohols with increasing basal spacings recorded from 13.2 to 14.0 Å as the carbon chain length increased. Complexes were also obtained for the C_2, C_4, and C_6 alcohols with basal spacings from 16.7 to 17.9 Å, indicating two layers of organic molecules lying in the interlamellar space with their lengths parallel to the silicate surfaces. They were able to obtain long-spacing complexes (26.5 to 41.0 Å) with temperatures above the melting points of the alcohols for C_6 to C_{18} alcohols and long-spacing complexes (34.2 to 58.6 Å) at room temperatures. Basal spacings measured at room temperature suggest that the alcohols were tilted in the interlamellar space at an angle of 77° to the silicate surfaces. Measurements taken above the melting points of the alcohols imply that a double-layer was formed with a portion of the chain rotated around the second or third carbon atoms and the extended part of the chain making an angle of 38.9° with the silicate surface.

Dowdy and Mortland (40) studied vapor phase adsorption of ethanol on homoionic Cu^{++}-, Al^{++}-, Ca^{++}-, and NH_4^+-montmorillonites. Application of infrared absorption techniques showed water of hydration on Cu^{++}-montmorillonite containing five percent water to be replaced as the clay was exposed to increasing pressures of ethanol. The moisture content was reduced to 0.6 percent at an ethanol pressure of $P/P_0 = 1$. Results indicated the presence of two types of water on Cu^{++}-montmorillonite: molecules coordinated directly to the cation and molecules in an outer coordination sphere or loosely adsorbed on the clay surface. X-ray data showed an expansion of the Cu^{++}-montmorillonite basal spacing to 13.3 Å, followed by rather stable basal spacings as exchange of ethanol for water occurred in the inner coordination sphere of the Cu ion. The final stage of adsorption was characterized by a further weakening of electrostatic bonding forces with a resultant expansion of the basal spacing to 16.5 Å. The basal spacing of 13.3 and 16.5 Å are in accordance with single and double layers of ethanol adsorbed in the interlamellar space with the CCO plane of ethanol parallel to the lattice surface.

Ca^{++}-montmorillonite exhibited a basal spacing of 16.5 Å but at a lower relative pressure of ethanol than that exhibited by the Cu^{++}-montmorillonite. Only a slight inflection occurred at a basal spacing of 13.4 Å in the plot of basal spacing versus relative pressure, indicating that Ca^{++}-montmorillonite does not have a preferred coordination habit that would encourage formation of a single layer of ethanol in the interlamellar space. At ethanol pressures of $P/P_0 = 1$, the Ca^{++}-clay lattice appeared to expand still further.

The Al^{+++}-, Na^+-, and NH_4^+-montmorillonite lattices did not expand beyond a basal spacing of 13.6 Å, showing no indication of formation of a double-layer of ethanol in the interlamellar spaces.

An extensive adsorption isotherm study was conducted by German and Harding (51) for a homologous series of primary aliphatic alcohols from aqueous solution with Na^+- and Ca^{++}-saturated montmorillonites. Their work concentrated on the influence of alcohol chain length, exchangeable cations and mineral surface on the adsorption equilibria of nonionic molecules from aqueous solution.

Amounts adsorbed were greater for the alcohols completely miscible with water (ethanol, n-propanol, and n-butanol) on the Na^+-montmorillonite. Adsorption isotherms obtained for Ca^{++}-montmorillonite showed the chain length of the adsorbate to have a more profound effect. Langmuir type adsorption isotherms were exhibited by the alcohols completely miscible with water and there was a slight increase in adsorption with increasing chain length. For the higher alcohols (n-pentanol to n-decanol), far too much sorbate was taken up in the interlamellar space of the Ca^{++}-montmorillonite to correspond to anything like a monolayer. Ca^{++}-montmorillonite adsorbed more alcohol than did the Na^+ form.

German and Harding (52), in an x-ray study of this same system, found a two-layer interlamellar adsorption of the C_1 to C_5 alcohols and a long-spacing series (26.8 to 34.0 Å) for C_6 to C_{10} alcohols adsorbed on Ca^{++}-montmorillonite. Na^+-montmorillonite showed a two-layer interlamellar adsorption for C_1 and C_2 alcohols, a one-layer adsorption for C_3 to C_6 alcohols, and a one-layer adsorption for C_7 to C_{10} alcohols, but only after a month of contact between the alcohols and the clay.

Amide interactions

Amides, derivatives of carboxylic acids in which the hydroxyl group has been replaced by the amino group, are reactive through electrons on either the oxygen atom or the nitrogen atom of the amide group. Early findings with adsorption of amides on montmorillonite suggested that protonation of the nitrogen atom occurred, but more recent works have provided theoretical, as well as experimental evidence, that protonation of the amides takes place through the oxygen atom.

Tahoun and Mortland (122) adsorbed acetamide, N-ethylacetamide, and N, N-diethylacetamide on H^+ and Al^{+++} saturated montmorillonite and utilized infrared absorption techniques to determine if amides become protonated on acid montmorillonite surfaces. Data reported suggested that acetamide was protonated on the surface of the H^+- and Al^{+++}-montmorillonites, but the protonation on the aluminum system was modified by the existence of a coordination reaction. N-ethylacetamide and N, N-diethylacetamide were more extensively protonated due to their more basic nature as a result of the effect of the one and two ethyl groups, respectively. Protons in the hydrogen system were from the exchangeable hydrogen ion, whereas, protons in the aluminum system came from highly dissociated water.

Aromatic interactions

Ion-dipole type van der Waals attractions are believed to influence the adsorption of aromatic molecules on montmorillonite. This type of interaction does not necessarily play an important role in the intercalation of nonpolar organic compounds, as such compounds are thought to be adsorbed on the interlamellar surfaces by induced dipole-induced dipole type van der Waals forces of attraction. Weakly polar molecules, such as nitrobenzene and phenol, replace the water associated with exchangeable cations and occupy the sites on the silicate surfaces previously taken up by the water molecules.

Barshad (15) found benzene capable of entering the interlamellar spaces of montmorillonite and vermiculite as long as the clays were partially hydrated. Bradley (20) and MacEwan (80) reported a double-layer interlamellar complex for benzene adsorbed on montmorillonite, with the plane of the benzene ring parallel to the silicate surface. Greene-Kelly (54) failed to achieve interlamellar adsorption of benzene on dehydrated montmorillonite.

Doner and Mortland (39) showed benzene and methyl-substituted benzene vapors to be intercalated by montmorillonite saturated with copper (II) cations. Mortland and Pinnavaia (92) found benzene to form two distinct complexes with montmorillonite depending upon the water content of the clay. At high water contents the benzene ring oriented itself parallel to the silicate surface, and at low water contents the benzene ring became tilted with respect to the silicate surface. They also investigated methyl-substituted benzenes, i.e. toluene, xylenes, and mesitylene adsorbed on copper (II) montmorillonite and found each of them to be both physically adsorbed on the montmorillonite basal planes as well as coordinated to the exchangeable Cu^{++} ion by copper (II) montmorillonite. Benzene and methyl-substituted benzenes formed a single-layer interlamellar complex, with the benzene ring more nearly parallel, than perpendicular, to the silicate surface.

Aldehyde and ketone interactions

MacEwan (80) reported a basal spacing of 13.2 Å for acetaldehyde adsorbed on halloysite, representing a single-layer of acetaldehyde adsorbed in the interlamellar space. Acetaldehyde did not penetrate the interlamellar space when reacted with montmorillonite under similar conditions.

Bissada, et al. (17) found a striking dependence of acetone adsorption on homionic montmorillonites on the nature of the exchangeable cation, suggesting that cation-dipole interactions play an important role in the adsorption process. At an organic solution concentration of 15 percent acetone formed a single-layer interlamellar complex with K^+-and Na^+-saturated montmorillonites with basal spacings of 13.4 and 13.2 Å, respectively, and a double-layer interlamellar complex with Ba^{++}-and Ca^{++}-saturated montmorillonites with basal spacings of 17.3 Å.

Parfitt and Mortland (103) found ketone adsorption by montmorillonite to be influenced by the nature of the exchangeable cation. Bonding mechanisms included: direct ion-dipole interaction of the carbonyl group with the exchangeable cation in cases where the cation had a low hydration energy or where special treatments were used to dehydrate the cation; outer sphere coordination to the cation by bridging through directly coordinated water molecules; formation of electrovalent bonds through proton donation by 2, 4 pentanedione to the montmorillonites saturated with Al^{+++} or Cu^{++} ions to form acetylacetonates of these ions. Acetone vapor formed a single-layer interlamellar complex with Na^+,

Ca^{++}, and Mg^{++} montmorillonites. Acetylacetone also formed single-layer complexes with the montmorillonites.

Interactions Between Montmorillonite and Aliphatic Amines

Montmorillonite, negatively charged, can be flocculated or precipitated by addition of water-soluble salts of amines or quaternary ammonium compounds. Often the montmorillonite can be redispersed by adding more organic salt, with the particles in the repeptized soil taking on a positive charge.

The exterior and interior basal plane surfaces of the montmorillonite exhibit a strong preference for organic cations. Initially, amine groups are adsorbed on the montmorillonite surface by exchange with exchangeable cations compensating for the excess of negative charge in the clay lattice. The hydrocarbon chains displace water from the montmorillonite surface causing the clay to lose its hydrophilic characteristics.

As additional organic salt is adsorbed by association of the hydrocarbon part of their molecule with that of the previously adsorbed ions, the ionic groups point toward the water phase. These ionic groups create a positive surface charge, and together with the anions of the amine salt form an electric double-layer that results in repeptization of the suspension.

Grim, et al. (60) were among the first to examine the reaction between montmorillonite and aliphatic amines. This particular study involved the adsorption of n-butylamine acetate, dodecylamine acetate, and ethyldimethyloctadecyl-ammonium bromide on montmorillonite. Their conclusions were that amines added in amounts less than the base-exchange capacity of the clay were adsorbed via base-exchange reactions. Amounts added in excess of the base-exchange capacity tended to be adsorbed by the action of van der Waals forces. The ability of clays to absorb water was greatly reduced after adsorption of the amine salts. N-butylamine ions, with the smallest molecular size of the salts used in the study, were not adsorbed in excess of the base-exchange capacity. The water content of the montmorillonite treated with dodecylamine acetate was generally less than the montmorillonites treated with the other two organic bases, which led to the conclusion that montmorillonite salts of organic cations adsorb less water than metallic ion salts adsorbed on the same clays.

Jordan (70, 71) studied the effect of amine chain length on montmorillonite basal spacings by adsorption of the salts for amines from propylamine to octadecylamine. His findings showed basal spacing of 13.6 Å for amines containing three to ten carbon atoms in the hydrocarbon chain and a basal spacing of 17.6 Å for amines having twelve to eighteen carbons in the chain. Jordan attributed these spacings to the formation of one and two layers of amines adsorbed in the interlamellar space of the montmorillonite, although later works refuted this concept.

Utilizing the assumption by Hendricks, et al. (65) that approximately eighty percent of the exchange positions of montmorillonite are on the basal plane surfaces, with the remainder on the broken-edges of the montmorillonite particles, Jordan computed an average area per base-exchange position on the basal plane in the order of 165 Å^2 for a montmorillonite having a base-exchange capacity of 100 milliequivalents per 100 grams. The basal plane areas covered by the adsorbed amines were calculated using this information and are reported in Table 2 (70). Gel volume measurements made by Jordan (70) when dodecylammonium-bentonite was immersed in various liquids suggest that approximately fifty percent coverage of basal plane areas was required for the development of a clay displaying a definite organophilic nature.

Cowan and White (33) showed in a study of the adsorption of aliphatic amines (ethylamine to n-dodecylamine) on montmorillonite that there was a gradual increase in tendency for an exchange reaction to occur from ethylamine to n-hexylamine. Between n-hexylamine and n-octylamine there was a marked transition wherein exchange of inorganic sodium ions was complete and some further mechanism of adsorption became operative.

Weiss (134) related basal spacing with charge density to refute previous findings by Jordan (70, 71) that had suggested a single layer of amines was adsorbed in the interlamellar space of montmorillonite with amines of up to ten carbon atoms in the hydrocarbon chain and two-layer complexes were formed with amines of longer chain length. Weiss showed that at low charge densities the hydrocarbon chains lie flat in

Table 2. Spatial relations for homologous alkylammonium bentonites (70)

Carbon Atoms In Chain	001 Spacings	Separation of[a] Clay Flakes	Layers of Amine	Calculated Amine Area	Calculated Area[b] of Clay Coated By Amine
	Å	Å		Å	%
0	9.6	0	0	0	0
3	13.5	3.9	1	38	23
4	13.4	3.8	1	44	27
8	13.3	3.7	1	69	42
10	13.6	4.0	1	81	49
12	17.4	7.8	2	94	57
14	17.4	7.8	2	106	64
16	17.5	7.9	2	119	72
18	17.6	8.0	2	131	79

[a] d_{001} spacings minus 9.6 Å.

[b] Calculated amine area divided by 165 $Å^2$ per base-exchange position.

the interlamellar space, but with increasing charge density the chains tended to overlap and to become erect. The basic conclusions of his work are evident from Figure 3 (134). This information, as well as findings by Barrer and MacLeod (10) and Barrer and Reay (14), brought a whole new dimension to the adsorption of amines on montmorillonite and subsequent adsorption of organic materials on the amine treated montmorillonites.

An extensive study of montmorillonite saturated with short-chain amine cations was performed by Diamond and Kinter (37). Their work concentrated on amines with hydrocarbon chains of less than four carbon atoms and included mono- to tetra-branching on the chains. Basal spacings measured showed montmorillonite saturated with any number of short-chain normal primary, secondary, or tertiary amines or quaternary ammonium cations formed complexes consisting of a monolayer of cations acting as "pillars" in the interlamellar space. Wet specimens and air-dried specimens resulted in regular basal spacings. Oven-drying caused a slight contraction in basal spacing ranging from 0.7 Å for the trimethylamine cation to about 0.1 Å for some of the other cations.

By adsorbing glycerol on Wyoming bentonite saturated with a series of short-chain aliphatic amine cations, Kinter and Diamond (77) were able to estimate the extent of interpillar area. The interpillar area, the total interlamellar area of the montmorillonite, and the number of amine cations present were used to calculate the area covered by individual cations adsorbed on the clay surface. They used 624 meters^2

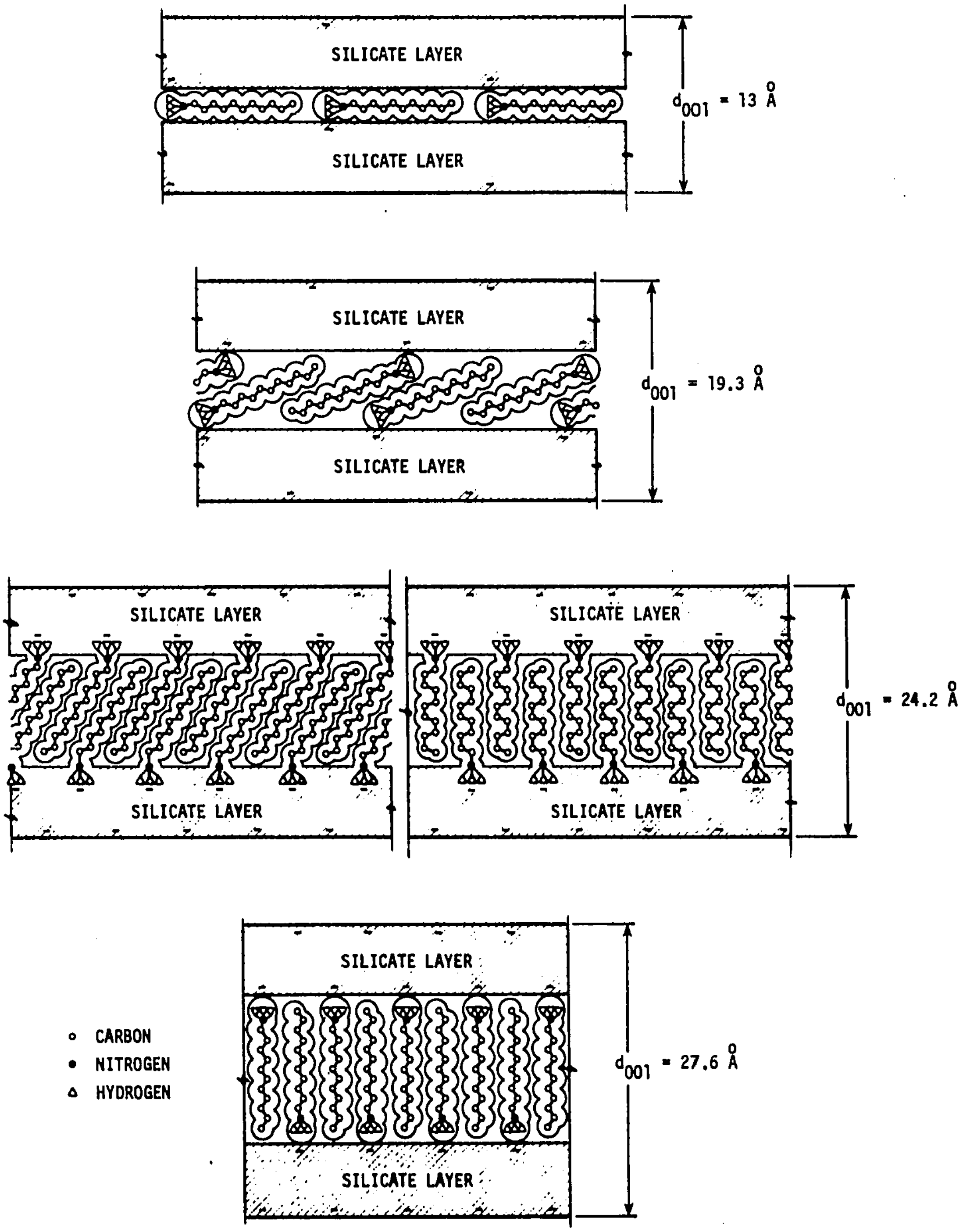


Fig. 3. Relation between basal spacing, charge density and arrangement of the alkyl chains in layer silicates with *n*-alkylammonium ions (134)

per gram for the interlamellar surface of the untreated clay, which is somewhat less than the 750 meters^2 per gram commonly associated with pure montmorillonite, but is reasonable for the bentonite used in their study. Data showed in all cases that the interlamellar surface area available to glycerol after the formation of amine cation pillars was substantially less than the interlamellar surface area available on untreated clay. Interlamellar area not covered by the amine pillars was estimated at 400 meters^2 per gram for methyl- and dimethlyammonium saturated clay, about 300 meters^2 per gram for ethyl-, trimethyl-, and tetramethylammonium, about 150-200 meters^2 per gram for diethyl- and di-n-propylammonium, and less than 50 meters^2 per gram for the larger tertiary amines and tetraethylammonium. Tri-n-butylamine adsorbed on the bentonite appeared to utilize the entire interlamellar area.

These findings were in accord with those of Cowan and White's study (34) for the adsorption of organics on ethylammonium to octadecylammonium bentonite. Cowan and White's work showed an increase in amine size was accompanied by a decrease in the amount of natural clay surface available for further adsorption. It should be noted, however, that adsorption of organics on amine treated clays occurs at both the hydrophilic surface of the natural clay and the hydrophobic portion of the amine molecules. Cowan and White found maximum adsorption of phenol on amine treated clays to occur when approximately equal amounts of each type of surface were available, which they found to be the case for dodecylammonium-bentonite.

N-alkylammonium and n-alkyldiammonium-montmorillonites prepared by Barrer and Millington (11) showed similar effects for the interlamellar space available for additional adsorption of organics after treatment with amine cations. The propylammonium-, dodecylammonium-, and dodecyldiammonium-montmorillonites of interest to this study showed basal spacings of 13.1, 14.6, and 13.4 Å, respectively. Assuming a value of approximately 9.4 Å for the basal spacing of untreated montmorillonite (similar to the 9.2 Å spacing shown in Figure 1 (129)), and using Pauling's value (104) of approximately 4.0 Å for the diameter of a CH_4 molecule, the basal spacings of 13.1 Å for propylammonium-clay and 13.4 Å for dodecyldiammonium-clay suggest the zig-zag of the hydrocarbon chains was lying flat between the silicate sheets of the montmorillonite. The zig-zag normal to the plane would actually require about 4.9 Å, but a recessing of each CH_2 group into the hexagonal hole of the oxygen ring in the tetrahedral surface by 0.45 Å would account for the difference. For dodecylammonium-clay, the area available per cation in a flat monolayer would not be sufficient, so some overlap of ions would occur, forcing the silicate layers further apart to give a partially rearranged organic layer. Although the dodecyldiammonium ion is similar in size to the dodecylammonium ion, it would tend to lie flat in the interlamellar space since the mean horizontal distance between negative charges on a tetrahedral surface is about 10 Å and the diammonium ion could satisfy pairs of uniformly spaced charges on the same surface.

Free interlamellar areas available after adsorption of the various alkylammonium and alkyldiammonium cations, as calculated by Barrer and

Millington, are presented in Table 3 (11). Calculations were based on an interlamellar area of 270 x 10^3 meters^2 per gram unit cell and allowed for an estimated four percent of the adsorbed amine cations to be located on external surfaces of the clay lattice. The values for methylamine and ethylamine are significantly lower than those reported by Kinter and Diamond (77). Discrepancies may be partly due to the fact that Kinter and Diamond used glycerol adsorption to determine free interlamellar space, whereas, Barrer and Millington's results were based on adsorption of nitrogen gas.

Interactions Between Alkylammonium-Montmorillonites and Several Organic Compounds

Jordan, et al. (72) noticed that a bentonite exhibiting high swelling properties in water showed an aversion to water and a tendency to swell in various organic liquids after reaction with appropriate organic ammonium salts. They found that an amine of more than ten carbon atoms was required for maximum gel strength in organic liquids, as measured by a grease cone penetrometer, for an amine treated bentonite. Gel strengths for dodecyl-, hexadecyl-, and octadecylammonium-bentonites were determined in mixtures of toluene with various normal primary aliphatic alcohols up to and including decylalcohol. Gel strength maxima occurred at low percentages of alcohol, with maxima occurring at progressively higher concentrations of alcohol with increasing molecular size of the alcohol. They concluded that adsorption of alcohols takes

Table 3. Calculated interlamellar free areas and volumes (11)

Cation	Gram Unit Cell Weight	Area Of Ion Å^2	Calculated Free Area (m^2/g.)	Calculated Free Vol. (cm.^{3}/g.)	Calculated Saturations (cm^3 at S.T.P./g.)	Observed Saturations (cm^{3}N$_2$ at S.T.P./g.)	$\frac{\text{Observed Saturation}}{\text{Calculated Saturation}}$
Alkylammonium Montmorillonites (c.e.c. = 85 meq. per 100 g.)							
$CH_3\overset{+}{N}H_3$	746	21.6	294	0.065	$41._7$	41.5	0.99
$C_2H_5\overset{+}{N}H_3$	755	29.8	214	0.073	$46._9$	35	0.74
$C_3H_7\overset{+}{N}H_3$	765	35.6	184	0.068	$43._7$	27.5	0.63
$C_4H_9\overset{+}{N}H_3$	774	41.4	155	0.060	$38._5$	12.5	-
$C_5H_{11}\overset{+}{N}H_3$	783	47.1	126	0.050	$32._1$	12.5	0.39
$C_5H_{13}\overset{+}{N}H_3$	792	52.9	98	0.039	$25._0$	3	0.12
Alkyldiammonium Montmorillonites (c.e.c. = 85 meq. per 100 g.)							
$\overset{+}{N}H_3(CH_2)_2\overset{+}{N}H_3$	746	34.8	278	0.078	$50._2$	-	-
$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$	750	40.6	262	0.092	$59._1$	43	0.86
$\overset{+}{N}H_3(CH_2)_4\overset{+}{N}H_3$	755	46.4	246	0.098	$62._9$	-	-
$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$	759	52.2	231	0.090	$57._8$	40	0.69
$\overset{+}{N}H_3(CH_2)_6\overset{+}{N}H_3$	764	58.0	216	0.082	$52._7$	-	-
$\overset{+}{N}H_3(CH_2)_7\overset{+}{N}H_3$	769	63.7	201	0.078	$50._2$	38	0.76
$\overset{+}{N}H_3(CH_2)_8\overset{+}{N}H_3$	773	69.5	187	0.073	$46._9$	29	0.62
$\overset{+}{N}H_3(CH_2)_9\overset{+}{N}H_3$	778	75.3	172	0.067	$43._0$	16	0.37

place through hydrogen bonding between the hydroxyl groups of the alcohols and oxygen atoms on the silicate surfaces of the bentonite.

Barrer and MacLeod (10) found that replacement of inorganic cations in montmorillonite by tetramethyl- and tetraethylammonium ions opened up the laminae of the clay, causing profound changes in the sorption and intercalation of organic molecules and greatly increasing the adsorptive capacity of the clay. In contrast to natural montmorillonites, paraffins and aromatic hydrocarbons were freely adsorbed between the laminae of the organic treated montmorillonite. Isotherm data showed selective adsorption of pentane in the order n-C_5H_{12} < iso-C_5H_{12} < neo-C_5H_{12}. Benzene was adsorbed more than n-heptane, which was adsorbed more than iso-octane.

Barrer and Reay (14) extended this work by examining the change in adsorptive capacity of montmorillonite treated with organic ions smaller than the tetramethylammonium ions. It was thought that adsorption of $CH_3NH_3^+$, $(CH_3)_2NH_2^+$, $(CH_3)_3NH^+$, and $(CH_3)_4N^+$ ions on montmorillonite would occupy relatively little interlamellar space, yet would cause sufficient separation of the clay laminae to allow the intercalation of additional small organic molecules. Basal spacings measured for montmorillonite treated with these four organic cations ranged from 12.0 Å for $CH_3NH_3^+$ to 13.5 Å for $(CH_3)_4N^+$. Several permanent gases and low molecular weight paraffins were adsorbed between the laminae of each of the methylammonium-clays. There was a marked decrease in affinity for large organic molecules from the $(CH_3)_4N^+$- to the $CH_3NH_3^+$-clays.

Investigating the adsorption of mono- and dihydric phenols on bentonite treated with n-aliphatic amines, ethyl- to octadecyl-amine, Cowan and White (34) found dodecylammonium-bentonite to be the most active member of the series. Increase or decrease in the size of the substituting amine tended to reduce the adsorptive capacity of the clay for the phenols in dilute aqueous solutions. Several factors were advanced as affecting the extent of phenol adsorption on the amine-treated clays. Alkylammonium-clays possess areas of both hydrophilic and organophilic properties, the balance between the hydrophilic clay surface and organophilic amine chains being critical; and the phenol molecules possess a localized center of high electron density, while the remainder of the molecule is essentially nonpolar. Cowan and White proposed that adsorption of the phenol on the amine-clays thus occurred by electrostatic hydrogen bonding between polar groups and by van der Waals bonding between organophilic centers.

Additional study of the phenol-amine clay system by Cowan (32) shed additional light on the adsorption mechanisms. Exploration of Freundlich adsorption isotherms and partial molar heats of adsorption showed phenol to be adsorbed in the interlamellar space of dodecylammonium-bentonite without a need for the clay lattice to undergo further expansion in order to accommodate the phenol molecules. Cowan postulated that this type of adsorption indicated the amine ions adsorbed on the interlamellar clay surface were the sites at which condensation occurred.

Slabaugh and Carter (114) examined the adsorption of methanol and nitrogen on Na^+-montmorillonites treated with aliphatic amines from n-butylamine to octadecylamine. Adsorption decreased for both adsorbates with increasing chain length of the adsorbed amines, except for dodecylammonium-montmorillonite which showed good adsorption of the methanol. These results further emphasized the idea that at about twelve carbon atoms the hydrocarbon chains of the amines begin to overlap, opening up more interlamellar area accessible to polar adsorbates but area apparently not accessible to nitrogen gas as an adsorbate.

Barrer and Millington (11) found the basal spacing of n-alkylammonium and n-alkyldiammonium treated montmorillonite to be determined by the adsorbate and to be little influenced by the valence or size of the organic exchange ion when the adsorbates were benzene and acetonitrile.

Stul, et al. (120) performed a quantitative study of the adsorption of n-aliphatic alcohols (butanol, hexanol, octanol, etc.) from dilute aqueous solutions on alkylammonium-montmorillonite as a function of the chain length of the cation and the alcohol, and as a function of the charge density of the clay. The interlamellar phase of the treated montmorillonite was found to act as a solvent, similar to the distribution of alcohol between alkane and water in bulk solution. Hydrogen bonds were suggested as a bonding mechanism between the hydroxyl groups of the alcohol and the ammonium groups of the alkylammonium ions. The exchange of water by alcohol on the interlamellar alkylammonium ions was considered the major factor in the transfer process. Adsorption was seen to increase with the chain length of the alkylammonium ions and with the number of these ions per unit cell. Increases in alcohol chain length also was accompanied by an increase in adsorption. Alcohol adsorption appeared to be more sensitive to alcohol chain length than to the chain length of the alkylammonium ions.

Stul, et al. (121) assumed that the interlamellar surface, the broken-edge surface, and the exposed basal plane surface corresponded, respectively, to 89.3, 6.46 and 7.24 percent of the total surface area of montmorillonite. Adsorption of alcohols on alkylammonium-montmorillonite was assumed to occur mainly in the interlamellar space. They found the minimum and maximum values for the basal spacing of alcohols adsorbed on dodecylammonium-montmorillonite shown in Table 4 (121). X-ray diffraction work carried out in the study brought forth an interesting concept. Integral and nonintegral d_{001} basal spacings showed a region of successive expansion of the clay laminae and was interpreted as a random interstratification of a two-component mixture. This led to a calculation of d_{002} basal spacings from a combination of d_{002} of the high-spacing compound and d_{001} of the low-spacing compound. The d_{001} basal spacings were taken from d_{001} values for the high-spacing compound. Similar results were obtained in this study but a different conclusion was advanced. The occurrence of high and low spacings was attributed to preferential adsorption.

Table 4. Minimum and maximum basal spacings for alcohols adsorbed on dodecylammonium-montmorillonite (121)

Alcohol	d_{min}, Å	d_{max}, Å
Ethanol	18.3	26.9
Butanol	18.6	29.6
Hexanol	19.9	28.2
Octanol	24.0	31.2

RESEARCH OBJECTIVES

Organic chemicals entering our nation's waters from both point and non-point sources have become a major environmental problem. The list of 129 priority pollutants in Appendix A (75) is the initial focus of massive efforts to monitor for the presence of and to find ways of removing these toxic chemicals.

Adsorption is the most widely used technique for removing organics from water and from wastewater after secondary wastewater treatment. Activated carbon is used almost exclusively. Granular activated carbon costs have risen and sell well in excess of $0.50 per pound for virgin carbon (61, 62). Both carbon and synthetic resin, another commonly utilized adsorbents, are derived from energy related sources. Clays have been recognized as adsorbents of organic materials for many years, but very few studies have been conducted to determine whether clays could be useful as adsorbents in the treatment of water and wastewater.

Bentonite, a colloidal clay, has been used as a coagulant in the purification of both water and wastewater (98, 99, 100). A few studies have been conducted using clays specifically as adsorbents of organics from water supplies (42, 89) and from wastewater (135), but except for the study by McBride, et al. (89) these studies have not attempted to alter the characteristics of the naturally occurring clay prior to using it as an adsorbent.

Much of the work reported in the literature review section dealing with interactions between alkylammonium-montmorillonites and several organic compounds suggests montmorillonite with the inorganic cations exchanged for alkylammonium ions may be a potentially effective adsorbent. Results obtained by Cowan and White (34) showed dodecylammonium-bentonite to be the best adsorbent, in a series of ethyl- to octadecylammonium-bentonites, for mono- and dihydric phenols. Slabaugh and Carter (114) reported good adsorption of methanol on dodecylammonium-montmorillonite. Stul, et al. (120) obtained good results for adsorption of alcohols on dodecylammonium-montmorillonite.

These findings for dodecylammonium-montmorillonite as an adsorbent, and suggestions by Weiss (134) that dodecyldiammonium ions form pillars in the interlamellar space of montmorillonite, led the author to choose these two alkylammonium ions for exchange on montmorillonite for this study. Propylammonium-montmorillonite was used in this study to provide a basis for determining the effect of amine chain length on the adsorption capacity of montmorillonite, and because Barrer and Millington (11) had calculated relatively high values for the free interlamellar volume of propylammonium-montmorillonite.

The specific objectives of this research were:

1. To remove the quartz, muscovite, and albite impurities from Wyoming bentonite to obtain the montmorillonite fraction of the clay.
2. To adsorb the chloride salts of aliphatic amines of various chain lengths (propylamine, dodecylamine, and dodecyldiamine) on the montmorillonite to expand the interlamellar space and to make clays of an organophilic nature to varying degrees.

3. To conduct adsorption isotherm studies for eleven organic compounds of interest to the water and wastewater field to determine whether they can be removed by the differently prepared montmorillonites.
4. To study the mechanism of attachment of the salts of the three aliphatic amines and the eleven organic compounds on the montmorillonite lattice structure.

ANALYTICAL TECHNIQUES

Many types of analytical equipment and procedures were used throughout the course of this research. The theory and practice associated with the equipment used most extensively are discussed to familiarize the reader with the major methods utilized. A brief synopsis of x-ray diffraction, gas chromatography, ultracentrifugation, differential thermal and thermogravimetric analysis, infrared spectroscopy, and scanning electron microscopy is presented. Other lesser used experimental methods are discussed in the appropriate sections describing procedures.

X-Ray Diffraction

X-rays are produced when fast-moving electrons impinge on crystalline matter. X-rays result from two general types of interaction of the electrons with the atoms of the target material:

1. A high-speed electron may strike and displace a tightly bound electron deep in the atom near the nucleus, thereby producing radiation characteristic of the target.
2. A high-speed electron may be slowed in passing through the strong electric field near the nucleus of an atom, with the decrease in energy of the electron appearing as an x-ray photon. X-radiation of this nature is independent of the target and is referred to as white radiation.

It is the characteristic radiation occurring in the range of 0.2 to 2.5 Å that is of interest to x-ray diffraction workers.

A part of the x-rays directed at a crystal lattice are scattered by electrons of the atoms in the lattice without change in wavelength. Such scattering produces a diffracted beam when certain geometric conditions are met. The diffraction pattern that results provides information about interplanar spacings, a complete set of which is characteristic for a specific mineral.

The x-ray diffraction unit used in this study was a Siemens D-500 diffractometer equipped with copper radiation, and is shown in Figure 4.

Gas Chromatography

Gas chromatography is used to separate and to identify volatile substances by passing a gas stream over a stationary phase. Columns varying from 0.01 up to 2.0 inches I.D. and from a few inches to more than fifty feet in length are filled with a packing material. Packings generally consist of an inert, size-graded solid support covered by a thin film of nonvolatile liquid solvent.

The sample is introduced as a plug into one end of the column in a controlled temperature environment and is carried through the column at a known flowrate under pressure by an inert carrier gas. The time required for the volatile substance to pass through the column is denotative of the substance. A detector indicates the presence of and measures the amount of various components in the sample appearing in the column effluent.

The gas chromatograph used in this study was a Hewlett-Packard,

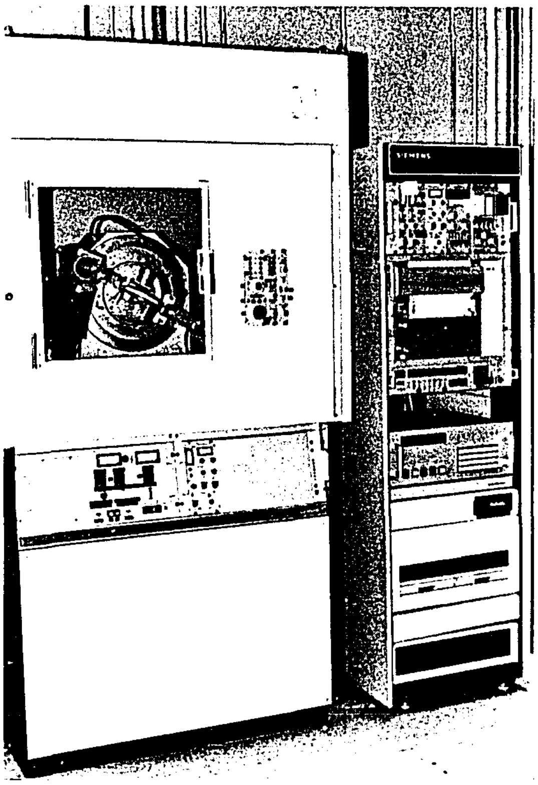


Fig. 4. Siemens D-500 diffractometer

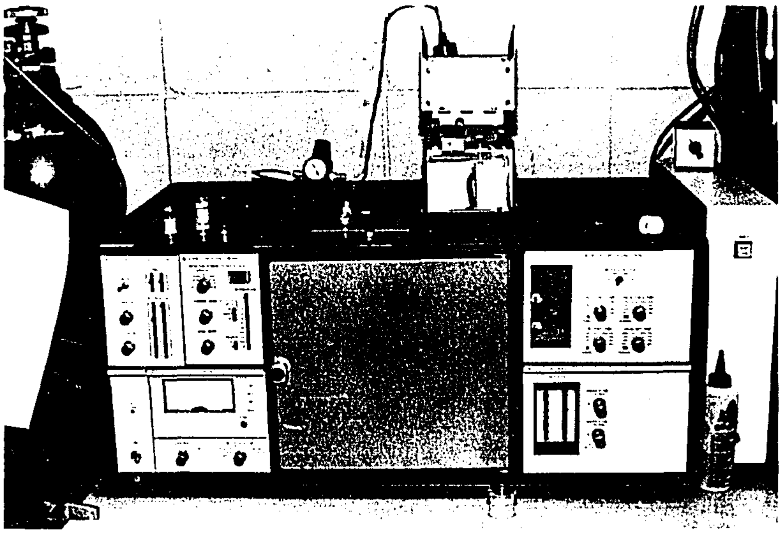


Fig. 5. Hewlett-Packard gas chromatograph, Model 5730-A.

Model 5730-A and is shown in Figure 5.

Ultracentrifugation

Centrifugation applies a separating force many times the force of gravity emanating from the center of rotation to a continuous flow of liquid containing solids. The centrifugal force for each of the particles in the liquid stream is defined by the following equation:

$$F = \frac{4\pi^2 mr}{T^2} \tag{4}$$

where

F = centrifugal force, dynes,

π = a constant with the numerical value 3.14

m = mass, grams

r = radius, cm

T = period of time required for one revolution of the column, seconds.

Since particles in the liquid are of different sizes and densities, and therefore different masses, they can be separated using this technique. The ultracentrifuge used in this study was a Sharples-Super centrifuge, Type M-41-22RY and is shown in Figure 6.

Differential Thermal and Thermogravimetric Analysis

Differential thermal (DTA) curves are plots of temperature against the instantaneous differences in temperature (measured with a thermocouple)

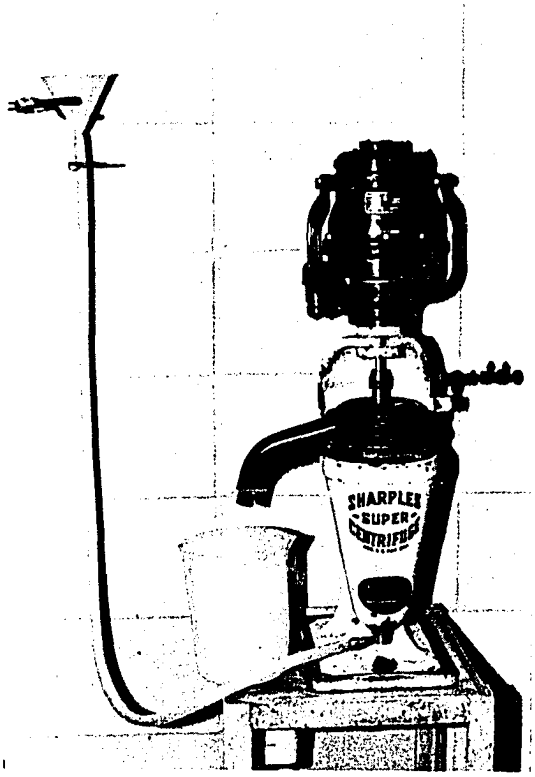


Fig. 6. Sharples-Super, flow through centrifuge

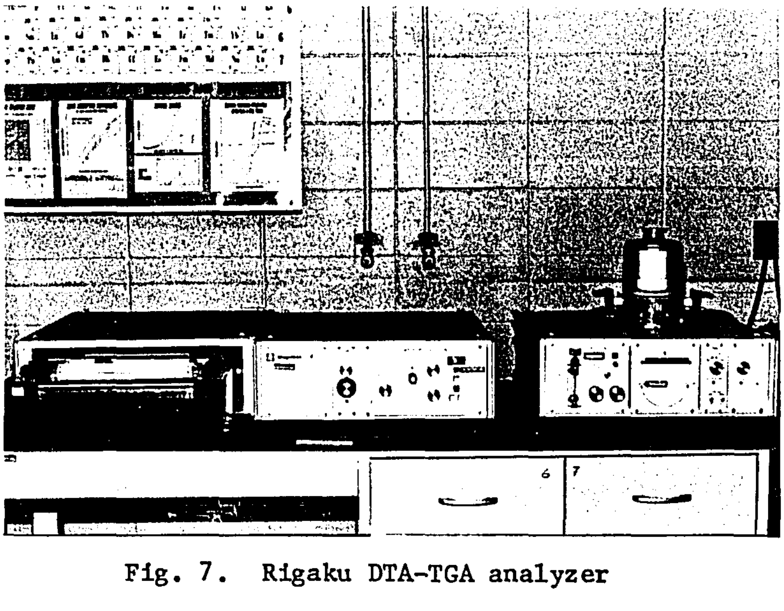


Fig. 7. Rigaku DTA-TGA analyzer

between a sample and a thermally inert material when the two materials are heated continuously to an elevated temperature in an enclosed furnace. Thermogravimetric (TGA) curves are plots of temperature against the instantaneous weight of the sample, also carried out in an environment of uniformly increasing temperatures.

In the case of clay minerals, differential thermal analyses show endothermic reactions due to dehydration and loss of crystal structure and exothermic reactions at the elevated temperatures as new phases are formed. The temperatures at which the reactions occur and the extent to which they occur are indicative of each type of clay, and to some degree can help identify idiosyncrasies within a given clay type. The strength of attachment of organics added to the montmorillonite structure can also be determined by measuring the temperature at which the organic material is burned off.

The differential thermal and thermogravimetric unit used in this study was a Rigaku model equipped with a platinum-rhodium thermocouple, Figure 7.

Infrared Spectroscopy

X-ray analysis is quite useful in determining long range ordering in crystals. Infrared spectroscopy provides a means for studying the order at the short ranges associated with neighboring atoms.

Atoms grouped together in molecules are continuously vibrating and rotating. Vibrations that are accompanied by a change in dipole moment give rise to the absorption of radiations in the fundamental infrared region of 2.5 to 20 micrometers wavelength (4,000 to 500 cm^{-1} wavenumber). Atoms of each molecule vibrate at a different frequency with respect to each other; the frequency being specific to the bonds in that molecule and useful for identification when detected by exposure to fundamental infrared radiation.

Since most mineral spectra have fewer absorption bands, and absorption bands that often occur at different wavelengths than the bands for organic spectra, infrared spectroscopy is also useful in determining chemical bonds that are formed when an organic material is adsorbed on clay or other mineral.

The infrared spectrophotometer used in this study was a Beckman-IR4 and is shown in Figure 8.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) utilizes a finely-focused beam of approximately 100 Å diameter to scan across small areas of the surface of the specimen. Secondary electrons, backscattered electrons, characteristic x-rays, and other types of radiation are released. Secondary electrons are collected to form an image on a cathode-ray tube. By varying the size of the area that is scanned on the specimen, magnification of the image can be varied from 15 to 100,000 times.

The SEM used in this study was a Japan Electron Optics Laboratory SEM, Model JSM-U3, and is shown in Figure 9.

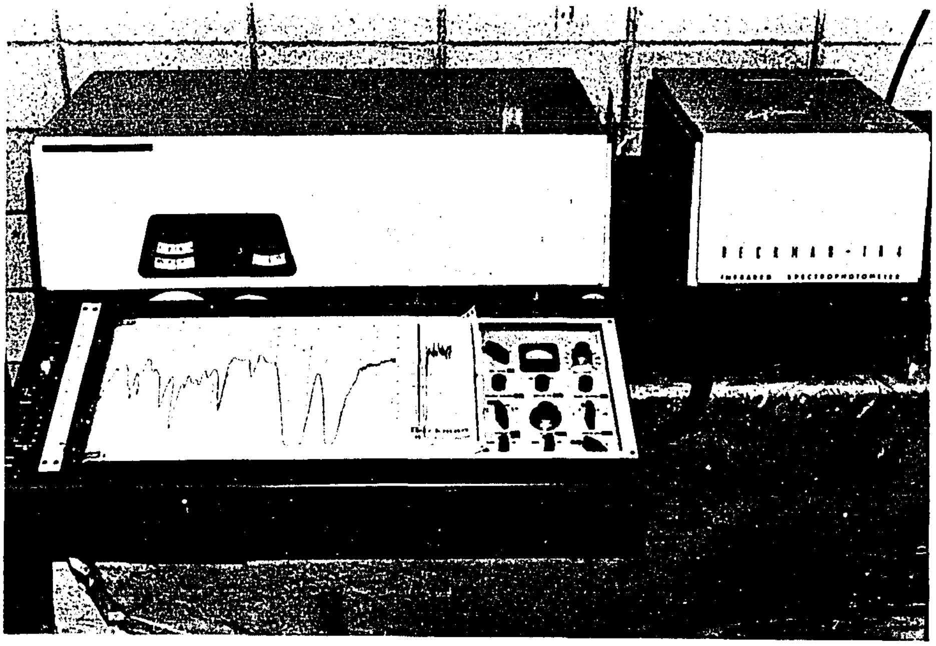


Fig. 8. Beckman-IR4 spectrophotometer

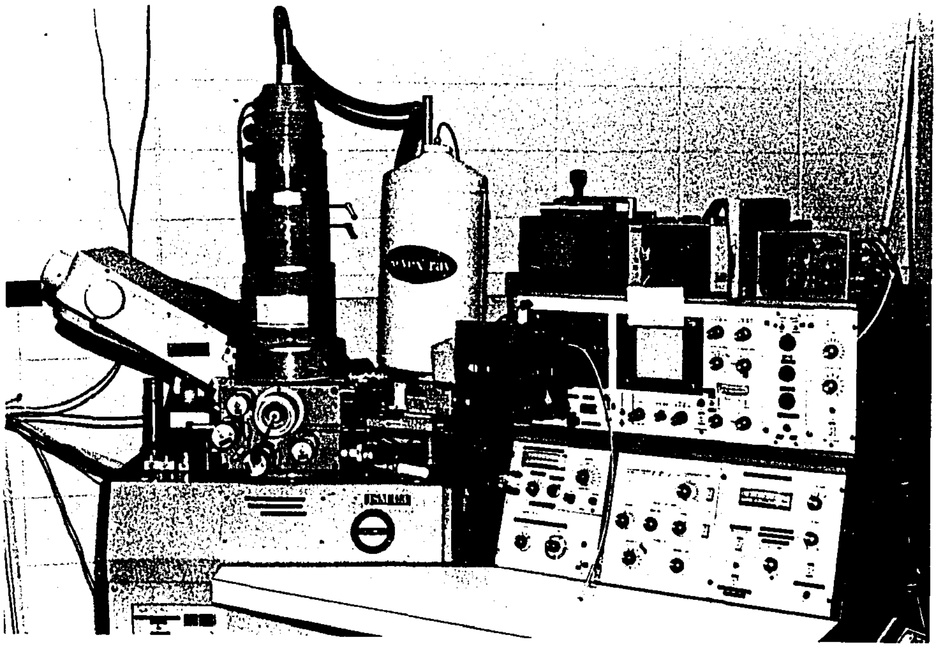


Fig. 9. Japan Electron Optics Laboratory SEM, Model JSM-U3

EXPERIMENTAL PHASE A

The first phase of experimentation was devoted to the separation of Na^+-montmorillonite from Na^+-bentonite, and the preparation of organically treated montmorillonites with the hydrochloride salts of propyl- and dodecylamine and dodecyldiamine.

The montmorillonite used was separated from a commercially available Wyoming bentonite known by the trade name Volclay-SPV and produced by the American Colloid Company. Demirel (36) reported the bentonite to be essentially a sodium-montmorillonite and ten percent other minerals; mainly feldspar, quartz, and volcanic glass.

The cation-exchange capacity of montmorillonites has been shown to vary from sixty-six to one hundred twenty-eight milliequivalents per hundred grams of sample, depending on impurities and chemical composition of the montmorillonite, but independent of particle size (41). Adsorption studies performed with montmorillonite, therefore, are highly influenced by the purity of the montmorillonite samples and care must be taken to remove any impurities if quantitative results are to be achieved with any degree of certainty.

X-ray diffraction patterns of the Wyoming bentonite were obtained on a Siemens D-500 diffractometer using monochromatic Cu $K\alpha$ radiation. Samples were run on air-dried, water saturated and ethylene glycol saturated bentonite, and the results are shown in Figure 10. Figure 10 shows several qualitative peaks indicative of the impurities present in the bentonite; the major ones being quartz, muscovite, and albite.

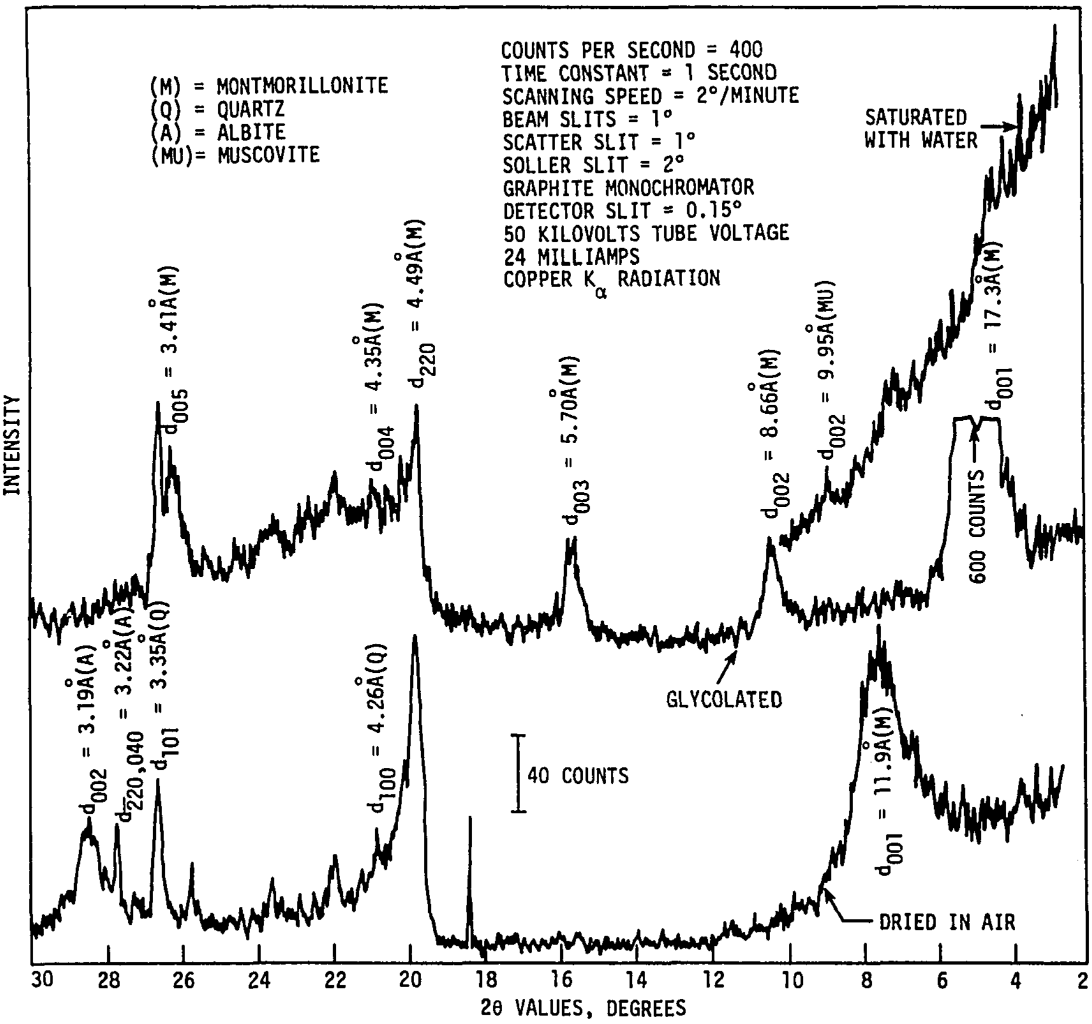


Fig. 10. X-ray diffraction patterns of Wyoming bentonite

The diffraction patterns in the Figure of the bentonite saturated with water and ethylene glycol reflect the fact that most of the montmorillonite is in the sodium form, although there may be some montmorillonite present in the calcium form based on results obtained by McAtee (85), with randomly interstratified mixtures of sodium and calcium montmorillonites.

Purification of Wyoming Bentonite

Several methods for separation of montmorillonite from bentonite have been advanced through the years. Essentially any separation technique is based on the force of gravity exerted by sedimentation procedures or on centrifugal force supplied by centrifugation. Purification was attempted originally by using sedimentation techniques and the detailed procedure used is outlined in Appendix B. This method was found to be inadequate and cumbersome for the removal of all of the quartz, muscovite, and albite impurities, and centrifugation was ultimately employed to separate the montmorillonite from the bentonite.

Procedures

A sample consisting of 150 grams of Wyoming bentonite was dispersed over a five-minute period in six liters of distilled water at seven hundred revolutions per minute using a Motomatic R motor generator manufactured by the Electro-Craft Corporation. Control of the revolutions was provided by a Cole Palmer constant speed and torque control unit. The suspension was stirred for approximately twenty-four hours at five hundred revolutions per minute to assure complete dispersion of the bentonite.

The suspension was then passed through a Sharples-Super-Centrifuge, Type M-41-24 2RY, under a centrifugal force equivalent to 13,200 times the force of gravity. The gravity feed rate of the suspension into the bottom of centrifuge column was approximately 130 milliliters per minute, although the rate varied as clay accumulated on the interior wall of the centrifuge column. Normally only two liters of suspension could be passed through the centrifuge before the system had to be shut down and cleaned.

The clay was removed from the interior wall of the centrifuge column and that from the lower quarter portion of the column was discarded as most of the impurities tended to accumulate there due to their size and density. Clay from the upper three quarters of the centrifuge column was redispersed in four liters of distilled water in the same manner as the original 150 grams of Wyoming bentonite had been dispersed. After another twenty-four hours of stirring at five hundred revolutions per minute, the suspension was run through the centrifuge again. The lower quarter of the column was discarded and the upper three quarters of the column was retained and used as montmorillonite.

Original intentions were to disperse the montmorillonite in a saturated solution of sodium chloride (5,500 milliequivalents of sodium per liter) to replace any Ca^{++}, Fe^{++}, or other exchangeable cations on the clay surface, but x-ray diffraction patterns of the montmorillonite samples indicated this procedure was not necessary.

After drying for several days, the montmorillonite was mechanically ground to finer than 200 mesh sieve size with a SPEX Industries, Incorporated, Metuchen, New Jersey, shatterbox grinder, Serial No. 1828. The cation-exchange capacity of the clay before and after purification was measured by the Iowa State University, Engineering Research Institute, Analytical Services Laboratory (ERI-ASL), using the procedures outlined in Appendix C. The cation exchange capacity was found to increase from approximately 72 milliequivalents per 100 grams of dry clay to 94 milliequivalents per 100 grams of dry clay when the material was nearly void of major impurities.

Results

Figure 11 presents the x-ray diffraction patterns for the clay collected in the top and bottom portions of the centrifuge column after passing the clay suspension through the centrifuge one and two times. The main quartz peak at a 2θ angle of 26.6°, d_{101}-spacing of 3.35 Å, diminishes greatly for the clay collected in the top portion of the centrifuge column. The majority of the albite appears to collect in the bottom portion of the column after only one pass of the clay suspension through the centrifuge; the main peaks being at 2θ angles of 28.0° and 27.8°, d_{002}- and $d_{\bar{2}20,040}$-spacings of 3.18 Å and 3.21 Å, respectively. Muscovite also appears to be largely removed in the discarded portion after only one pass through the column as its diffraction peak at a 2θ angle of 8.9°, d_{002}-spacing, quickly diminishes in intensity.

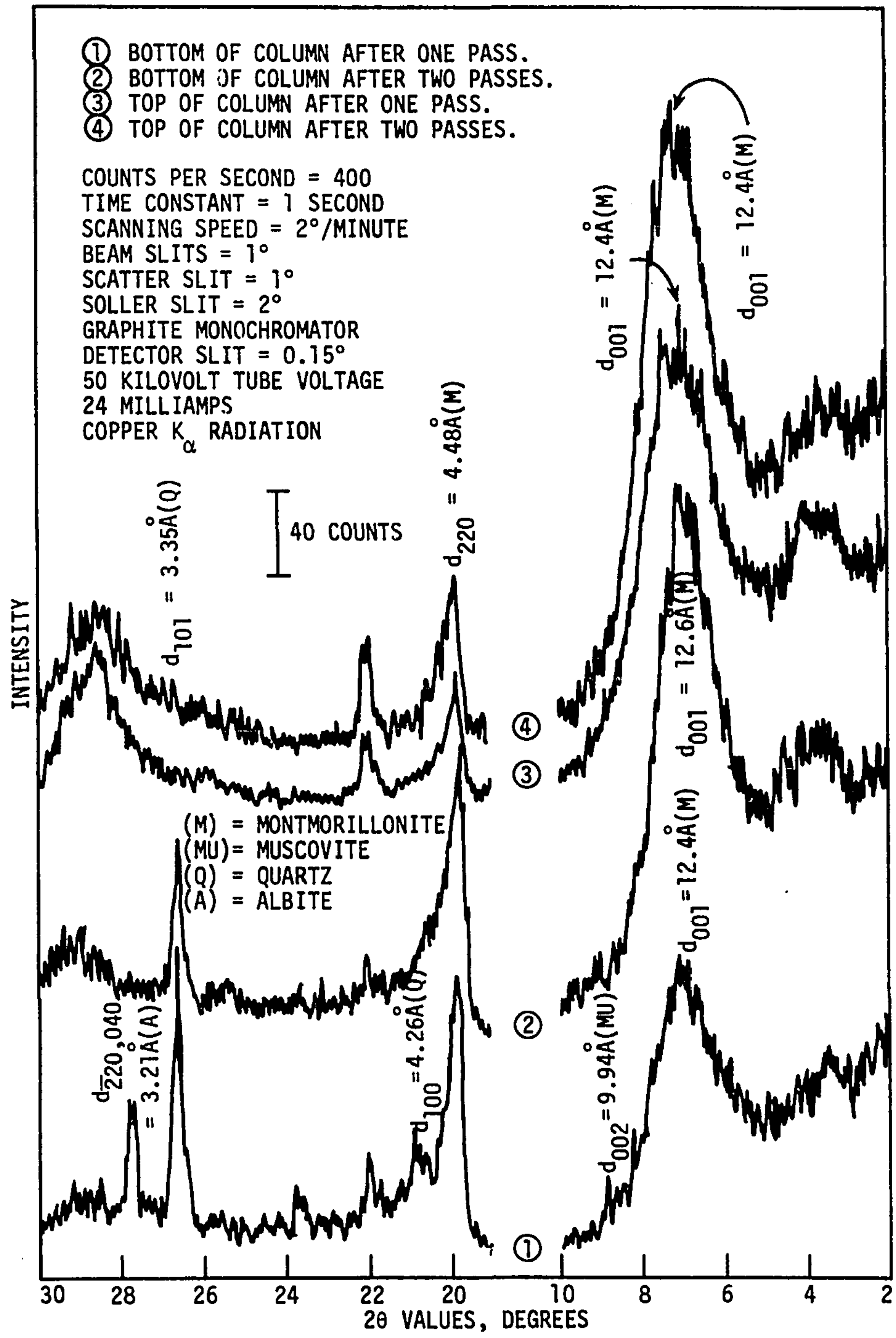


Fig. 11. X-ray diffraction patterns of different fractions of centrifuged Wyoming bentonite

The x-ray diffraction patterns generally indicate that the clay collected in the top portion of the centrifuge column after passing the clay suspension through once would be sufficiently void of unwanted impurities, but the clay suspension was centrifuged a second time to insure availability of a fairly pure montmorillonite fraction for further experimentation.

Differential thermal analysis (DTA) and thermogravimetric (TGA) curves for Wyoming bentonite and the montmorillonite fraction are presented in Figure 12. The only noticeable differences between the two materials are the slight quartz inversion on the DTA curve for Wyoming bentonite and the larger endothermic peak for the desorption of interlayer water that occurs at a higher temperature on the DTA curve for the montmorillonite. Both materials exhibit an endothermic peak at 740 C, corresponding to dehydroxylation, or loss of hydroxyl groups from the octahedral layer in the form of water. The endothermic peaks at 935 C indicate loss of the last traces of hydroxyl water from the tetrahedral layer or the breakdown of the montmorillonite structure. The exothermic peaks at 975 C and 990 C are a result of the recombination of the elements in the structure to form oxides.

Figure 13 is the scanning electron micrographs obtained for Wyoming bentonite and the montmorillonite fraction. Although the difference in levels of quartz, muscovite, and albite are not ascertainable from the micrographs, the smaller size of the montmorillonite particles due to the grinding to which it was subjected is somewhat noticeable.

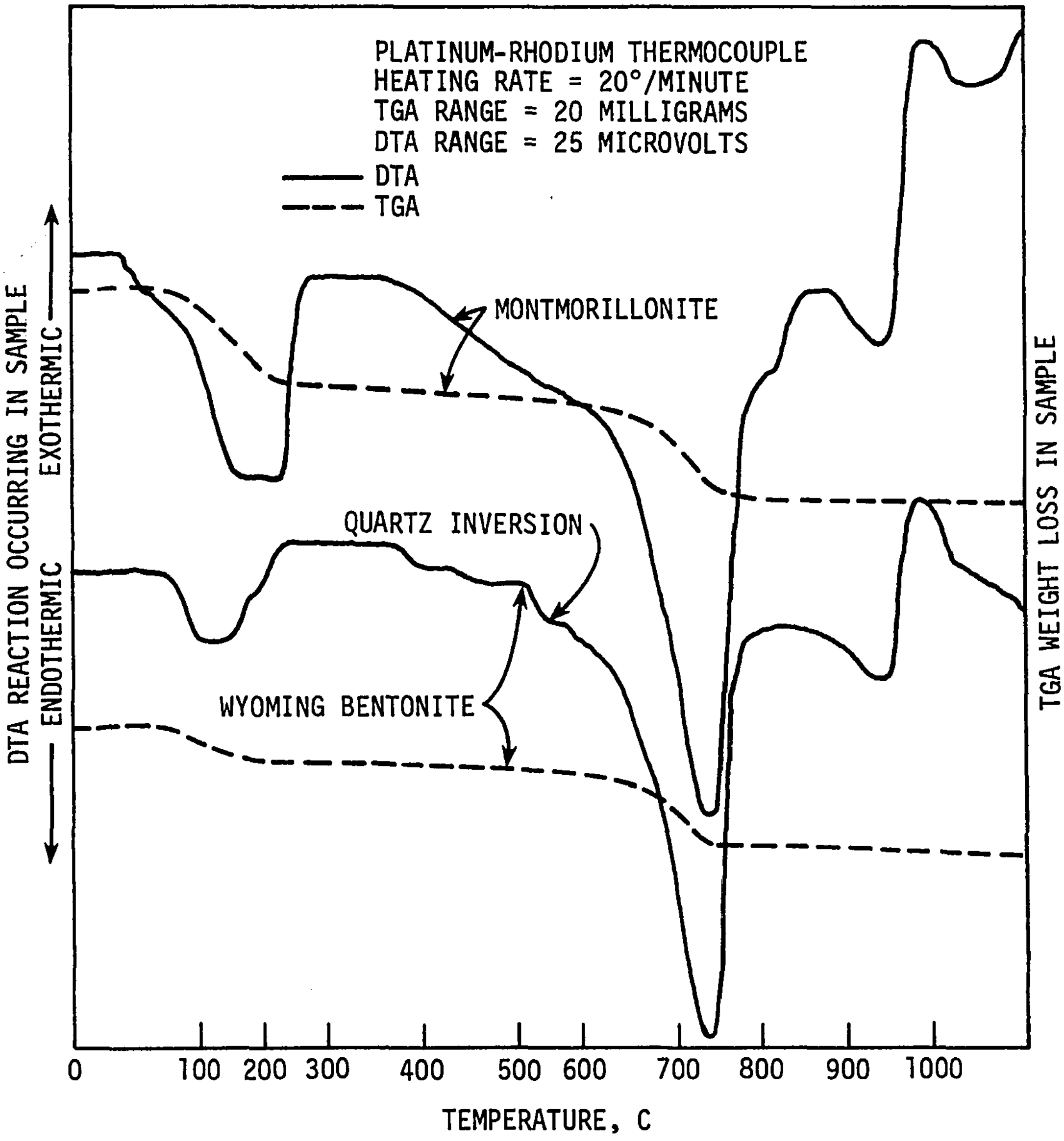
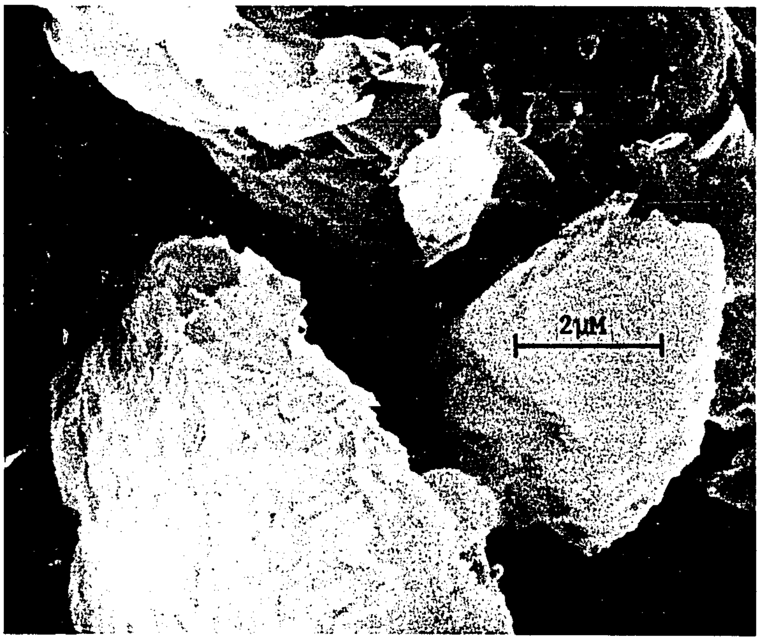
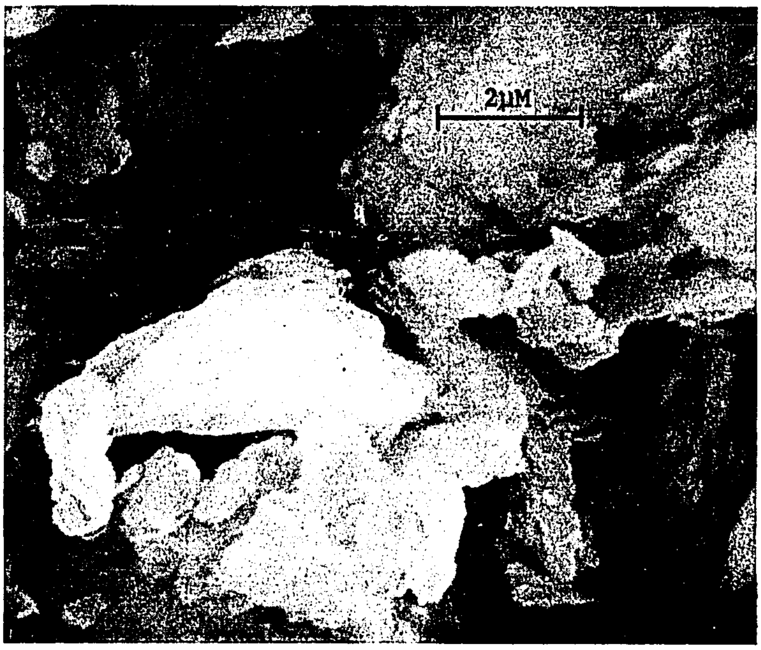


Fig. 12. DTA-TGA curves of Wyoming bentonite and the montmorillonite fraction



a) Wyoming bentonite



b) montmorillonite

Fig. 13. Scanning electron micrographs of Wyoming bentonite and the montmorillonite fraction; 10,000 X

Discussion

Sedimentation procedures in Appendix B were initially employed to separate the montmorillonite from Wyoming bentonite. These procedures were found to be inadequate for the removal of quartz, muscovite, and albite impurities and centrifugation techniques were used. X-ray diffraction patterns showed the clay collected in the upper three quarters of the centrifuge column to be mainly sodium montmorillonite since the wet sample showed complete expansion. Removal of quartz from the bentonite by centrifugation was further verified by DTA curves. The shape of the DTA curves for loss of interlayer water confirmed the fact that the majority of the montmorillonite was in the sodium form since a single endothermic peak was observed. Calcium montmorillonite typically exhibits two peaks, one peak for free interlayer water and another peak associated with bound interlayer water.

Adsorption of Three Aliphatic Amine Salts on Montmorillonite

The hydrochloride salts of propylamine, dodecylamine, and dodecyldiamine were adsorbed on the purified montmorillonite. The dodecylamine and dodecyldiamine were 99 percent pure and were purchased from Pfaltz and Bauer, Inc., Stamford, Connecticut. Propylamine was purchased from the Eastman Kodak Company, Rochester, New York.

Selection of three amines provided a basis for determining the effect of the adsorbed hydrocarbon chain length on the properties of the montmorillonite. The effect provided by monovalent versus divalent cations was also discernible since one of the dodecylammonium ions was an amine and the other was a diamine.

Procedures

Although propylamine (a liquid) is readily soluble in water (119, 131, 133), dodecylamine and dodecyldiamine (solids) are essentially insoluble (28, 67, 109, 131, 133). For this reason, and because the exchange of charge compensating inorganic cations on the clay surface is accomplished with organic cations, the hydrochloride salts of the amines were interacted with montmorillonite.

The hydrochloride salt solutions were prepared by mixing the appropriate amount of amine with hydrochloric acid solutions with normalities ranging from 0.04 to 0.08 N. The hydrogen ion concentration used was approximately twenty percent in excess of that necessary for interaction with the amines, and the amines were mixed with the acid solution for about twenty-four hours, to assure that all of the amine was converted to its chloride salt form.

Adsorption of the alkylammonium salts on the montmorillonite was carried out in 250 milliliter conical flasks. A two gram sample of dessicated montmorillonite was added to each flask. One hundred milliliters of liquid sample was then added to each flask with various quantities of distilled water and alkylammonium salt solution making up the liquid portion, depending on the concentration of amine salt desired in each flask. Amine salt concentrations in the flasks ranged from twenty-five to five hundred percent of the cation-exchange capacity of the montmorillonite. The flasks were stoppered and placed in a mechanical shaker (Water-Bath Shaker by Eberbach Corporation, Ann Arbor, Michigan) in a constant temperature room at 20 C for forty-eight hours.

The clay from each flask was separated from the liquid by batch centrifugation at five thousand revolutions per minute using an IEC centrifuge, (Universal Model UV, by the International Equipment Company, Needham, Hts., Massachusetts). The clay was dried in an oven at 60 C, mechanically ground to less than 200-mesh sieve size, and analyzed by x-ray diffraction, differential thermal and thermogravimetric analysis, and infrared spectroscopy to ascertain the effects of the adsorption of the alkylammonium cations on the properties of the montmorillonite.

A sample of the clay from each flask was then added to a liter of distilled water and mixed using the mechanical shaker for twenty-four hours to remove excess physically adsorbed ammonium salt. The clay was separated from the wash water by batch centrifugation and subjected to the same analytical procedures as the unwashed clay.

Samples for infrared absorption analysis were prepared by grinding and mixing approximately 5 mg of desiccated clay with 400 mg of potassium bromide powder, KBr. The mixture was ground again after saturating it with ninety-five percent ethanol to drive off unwanted moisture. The sample was dried in an oven at 60 C for twenty-four hours, and then compressed at 76,000 pounds per square inch of pressure for fifteen minutes to form a translucent pellet approximately 1 mm thick. The pellet was scanned from 1.0 to 15.0 μm in the double-beam mode on a Beckman IR-4 infrared spectrophotometer. The sample in the reference beam was a pellet made from 400 mg of KBr with no clay added.

The two grams of montmorillonite originally added to each flask could not be recovered completely for washing, so an estimate of the montmorillonite and ammonium salt fractions of the recovered, unwashed clay had to be determined. Calculations used to determine these fractions were based on the weight of the recovered alkylammonium-montmorillonite and the amount of ammonium salt adsorbed per gram of montmorillonite. The results of a sample calculation are presented in Appendix D.

Samples of the solution liquid and the wash water were analyzed for amine content with a Beckman carbon analyzer, model 915-A. Analysis was performed by the ERI-ASL. Total carbon was measured by combustion IR, and inorganic carbon was measured by low temperature IR so it could be subtracted from the total carbon value to give the organic carbon value associated with the amine. Originally, the liquid sample was to be analyzed by performing a Kjeldahl digestion and using an Orion Research ammonia electrode, model 95-10, to measure ammonia content. Excessive foaming was encountered with dodecylammonium chloride solutions during the Kjeldahl digestion procedure and this method was abandoned.

Results

The adsorption and x-ray diffraction data from several experiments in which various amounts of dodecylammonium, dodecyldiammonium, and propylammonium salts were added to two gram samples of montmorillonite are presented in Figures 14a and b, 15a and b, and 16a and b, respectively.

Figures 17a, b, and c, show these data plotted according to the Brunauer, Emmett, Teller (BET) isotherm model for apparent multilayer adsorption.

The regression lines fitted to the data for the alkylammonium-montmorillonites in Figure 18 demonstrate the ability of the three alkylammonium ions to remain attached to the montmorillonite lattice after washing each two gram sample in one liter of distilled water.

Figures 19a and b, show the x-ray diffraction patterns of the dodecylammonium-, dodecyldiammonium-, and propylammonium-montmorillonites before and after washing off the excess physically adsorbed amines.

The DTA-TGA curves for the dodecylammonium-, dodecyldiammonium-, and propylammonium-montmorillonite after washing off excess physically adsorbed amines are presented in Figure 20. Figure 21 shows the DTA-TGA curves for dodecylammonium-montmorillonite before and after washing off the excess physically adsorbed dodecylammonium-salt.

The scanning electron micrographs of the three alkylammonium montmorillonites, at a magnification of 10,000 X, are presented in Figure 22.

Infrared absorption spectra of dodecylamine, dodecyldiamine, and propylamine are presented in Figure 23 (107). Also, shown in Figure 23 are characteristic absorption band positions in mineral spectra, of which many apply to montmorillonite. Figure 24 shows the infrared absorption spectra obtained for the three alkylammonium-montmorillonites and the untreated montmorillonite used in this study.

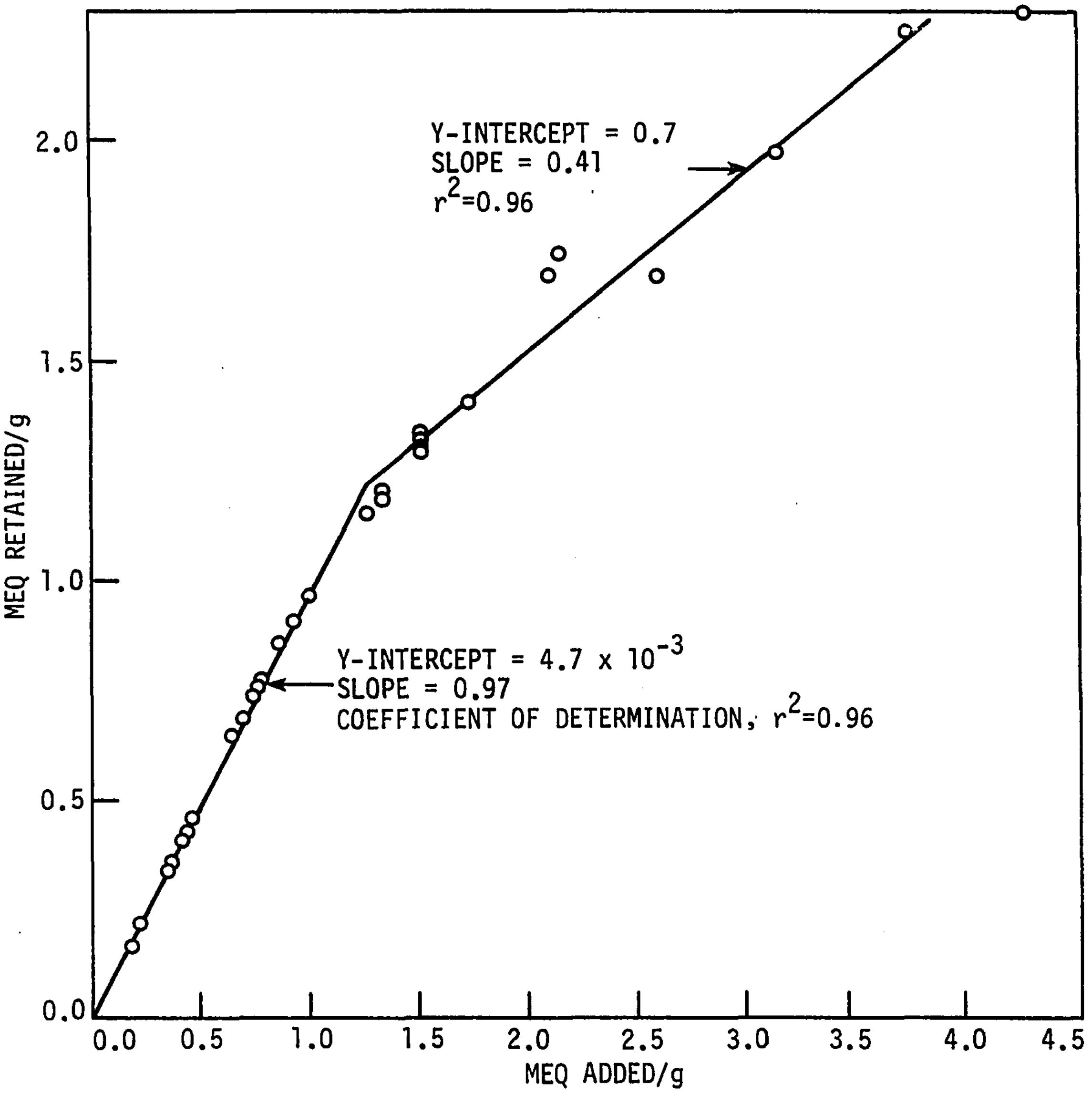


Fig. 14a. Milliequivalents of dodecylamine retained per gram of montmorillonite versus milliequivalents of dodecylamine added per gram of montmorillonite

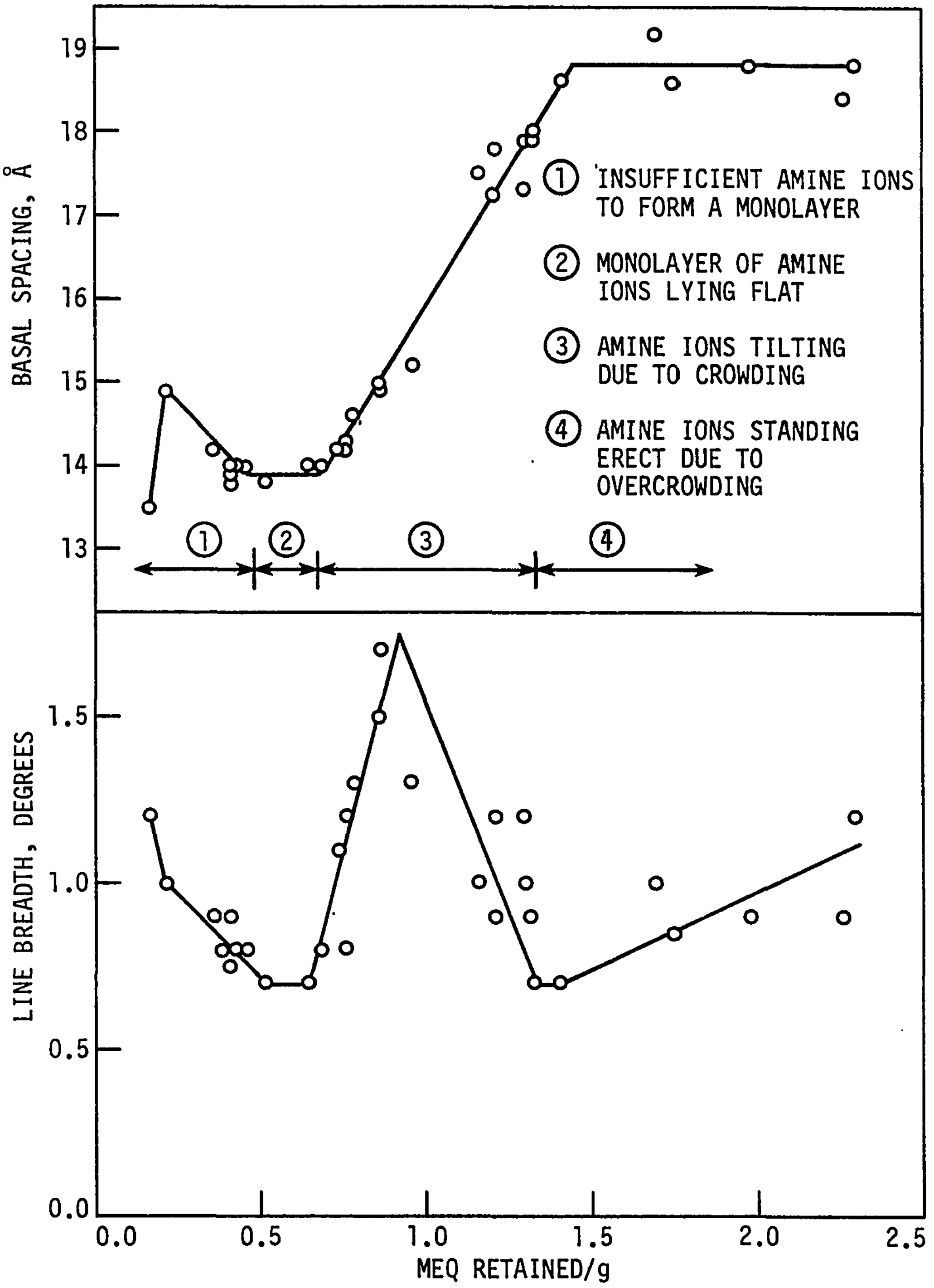


Fig. 14b. Basal spacing and line breadth versus milliequivalents of dodecylamine retained per gram of montmorillonite

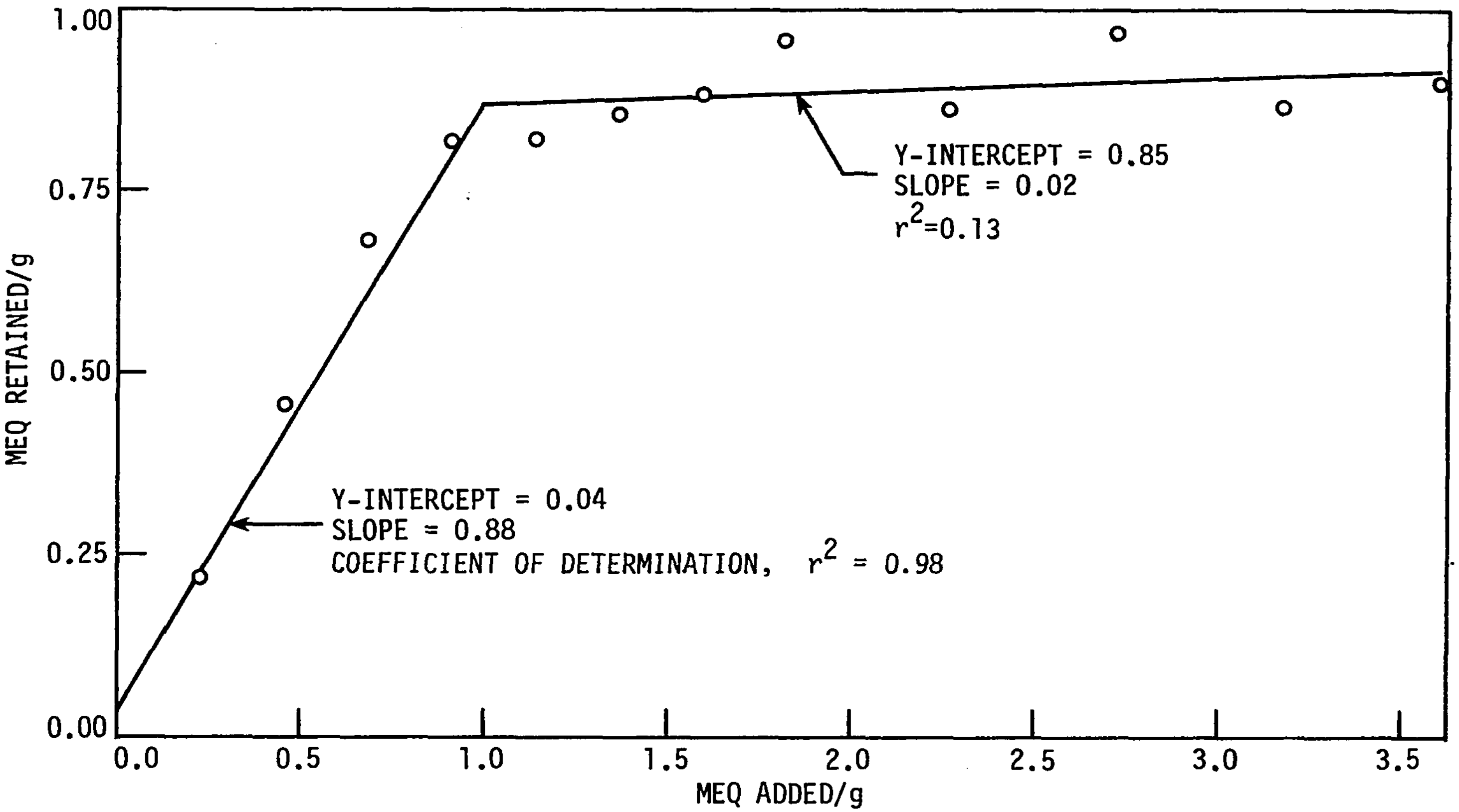


Fig. 15a. Milliequivalents of dodecyldiamine retained per gram of montmorillonite versus milliequivalents of dodecyldiamine added per gram of montmorillonite

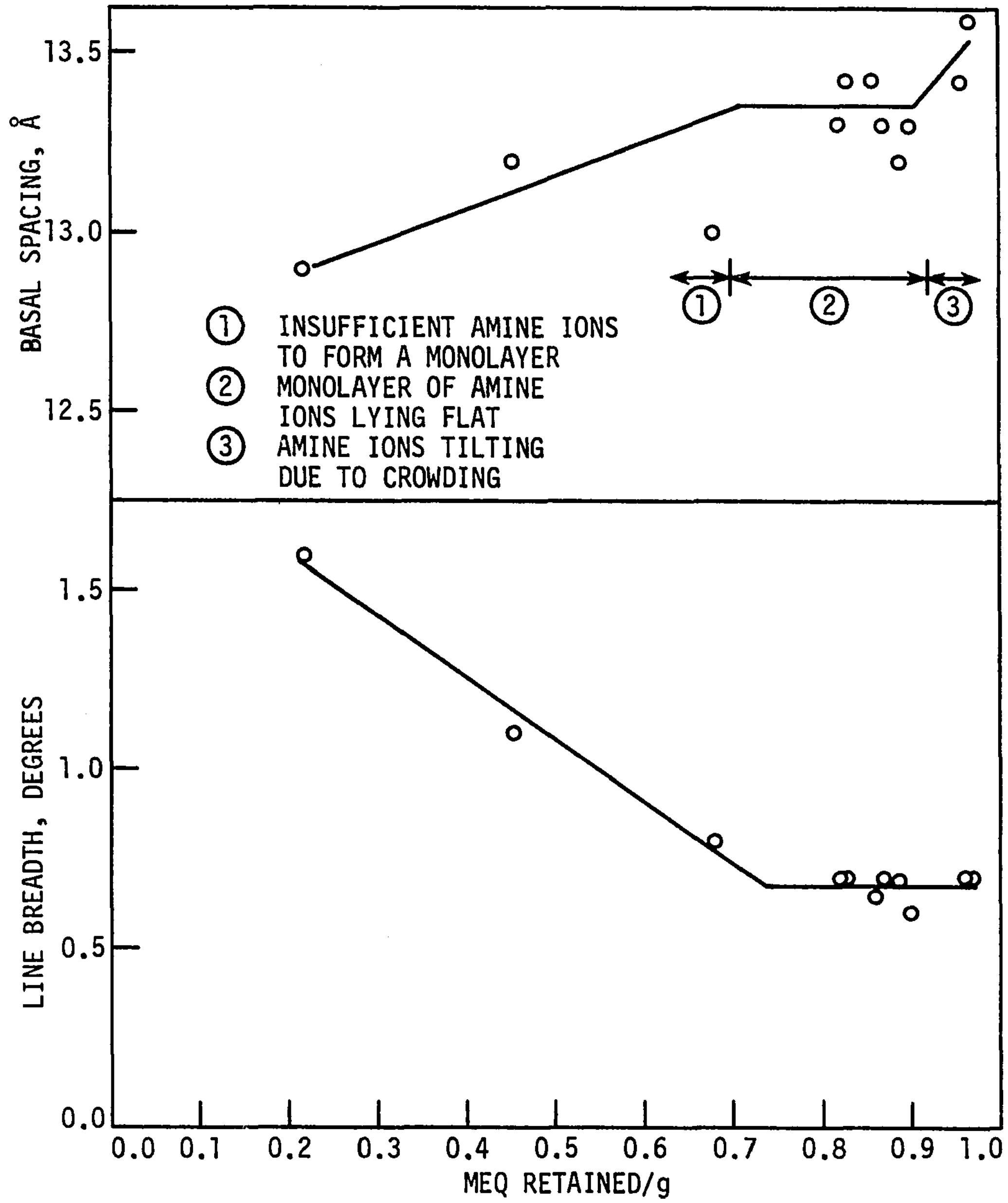


Fig. 15b. Basal spacing and line breadth versus milliequivalents of dodecyldiamine retained per gram of montmorillonite

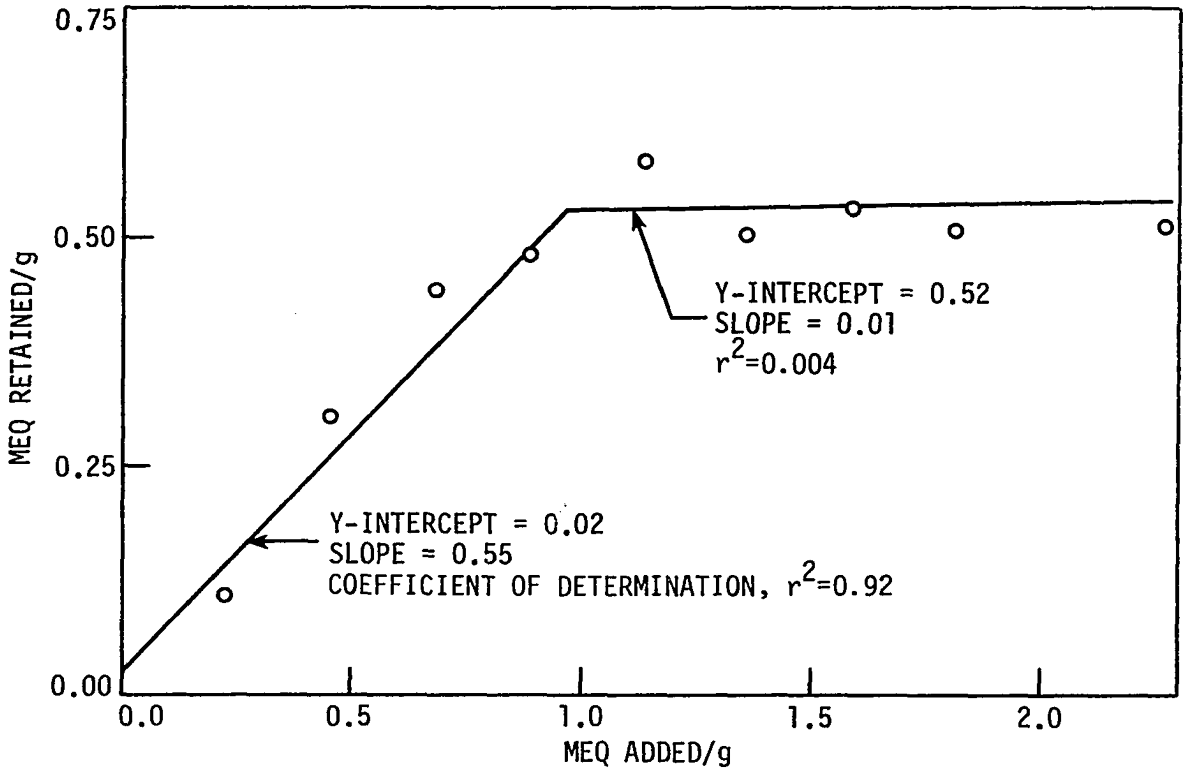


Fig. 16a. Milliequivalents of propylamine retained per gram of montmorillonite versus milliequivalents of propylamine added per gram of montmorillonite

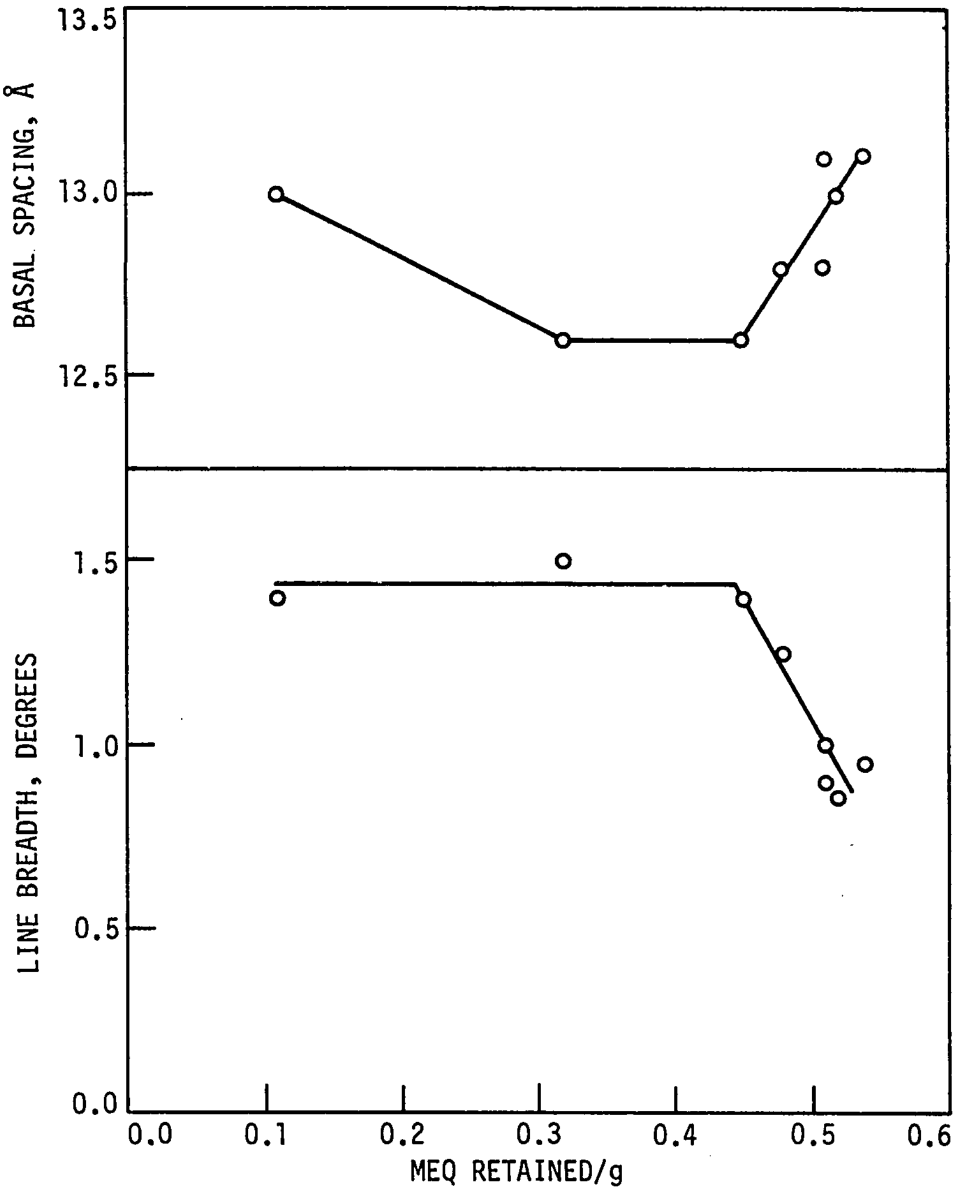


Fig. 16b. Basal spacing and line breadth versus milliequivalents of propylamine retained per gram of montmorillonite

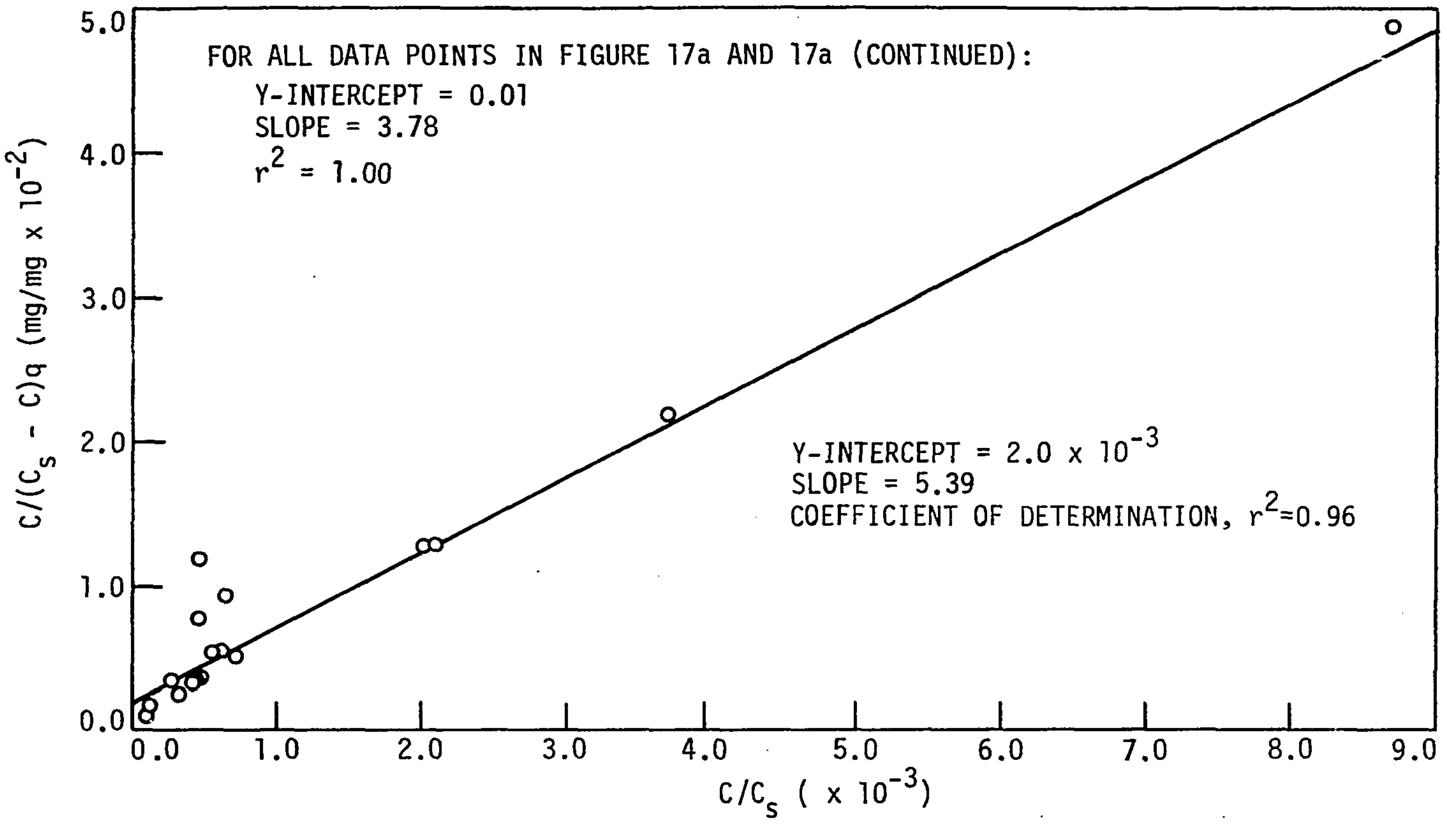


Fig. 17a. BET plot of dodecylamine retained on montmorillonite

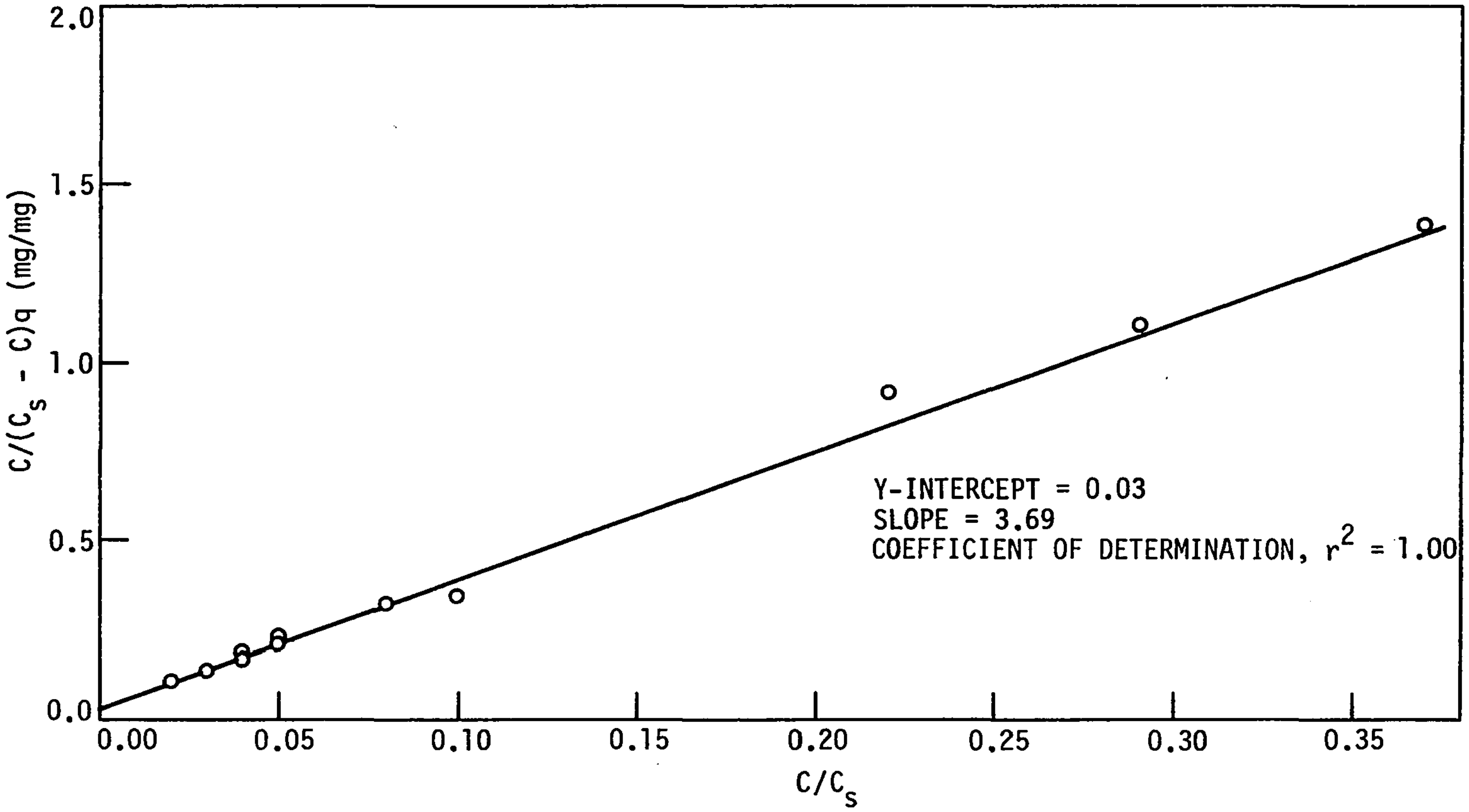


Fig. 17a. (Continued)

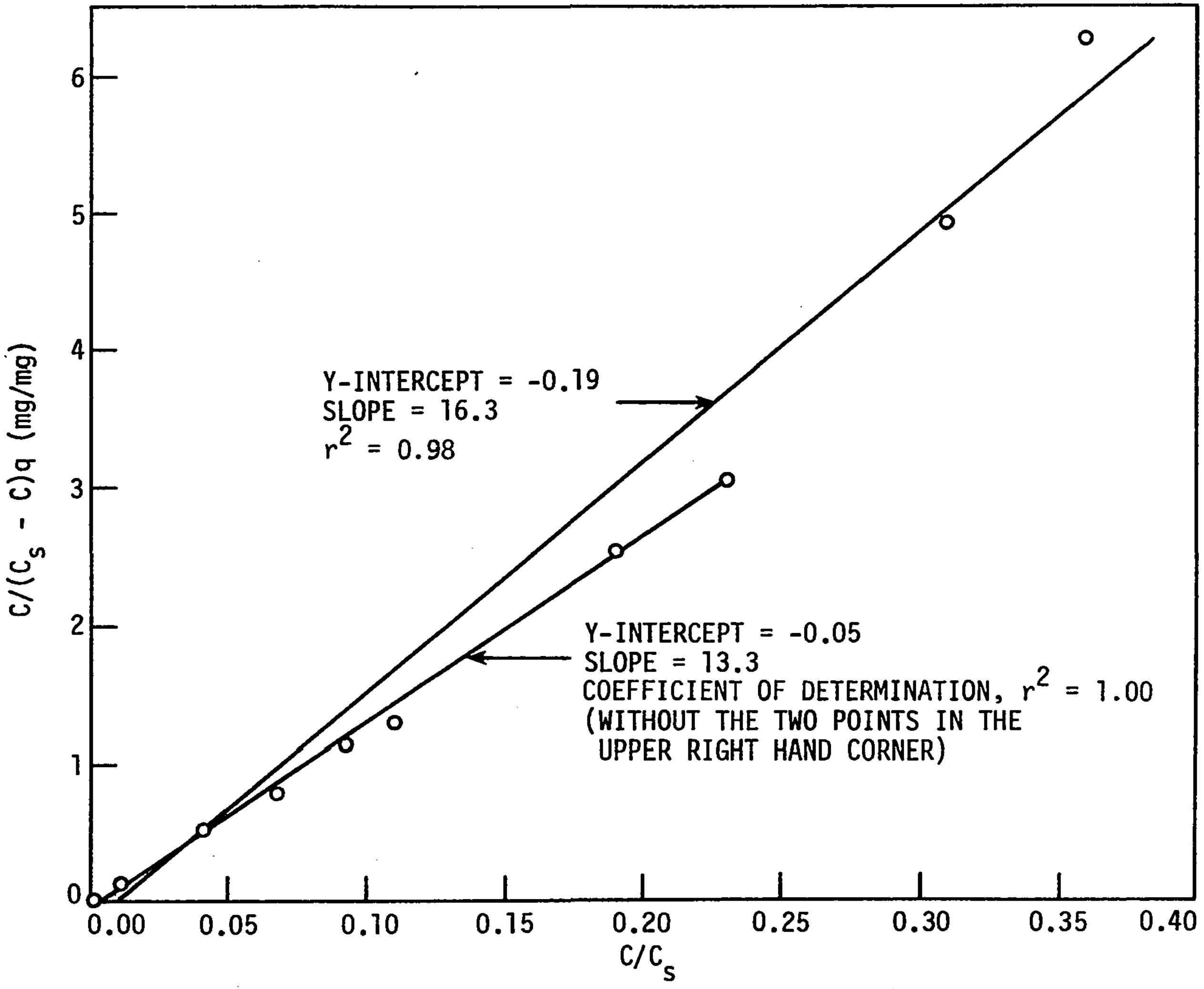


Fig. 17b. BET plot of dodecyldiamine retained on montmorillonite

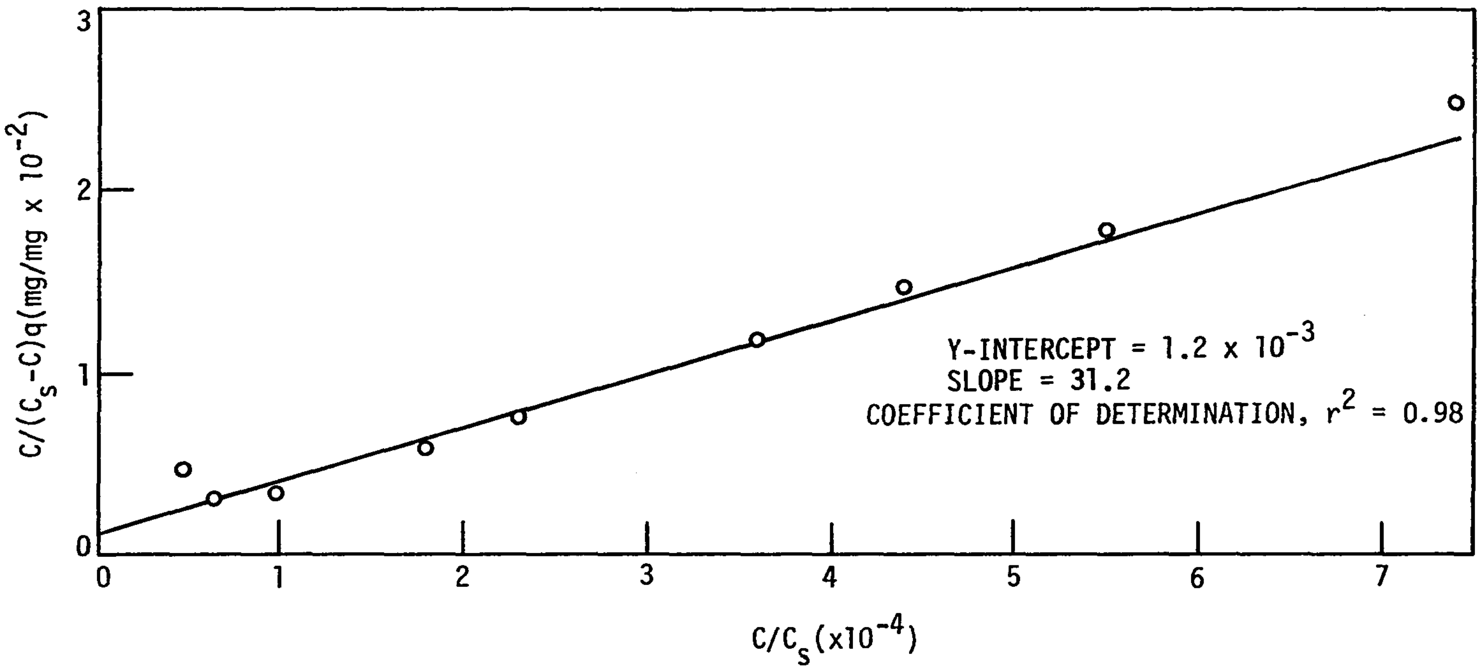


Fig. 17c. BET plot of propylamine retained on montmorillonite

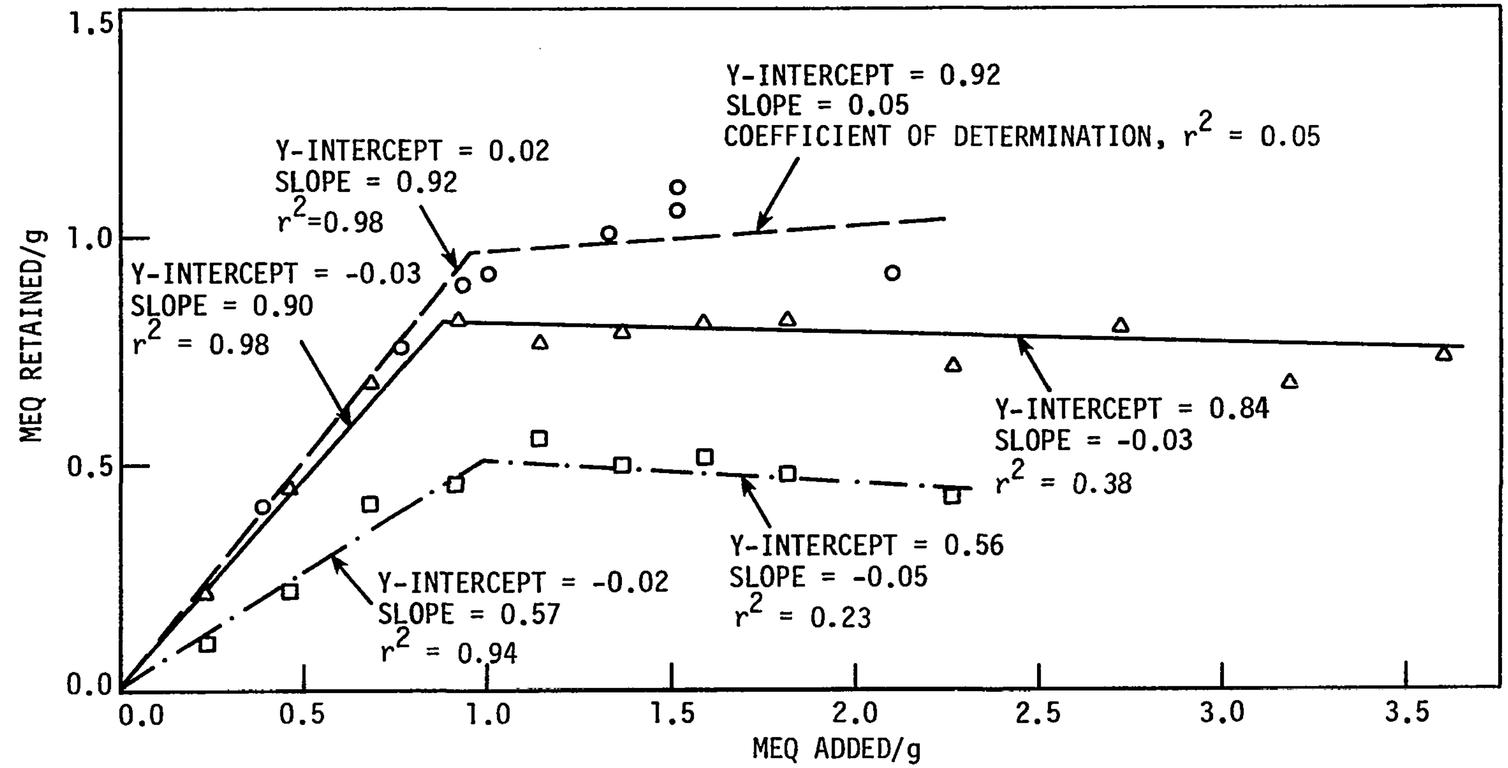


Fig. 18. Milliequivalents of dodecylamine (○), dodecyldiamine (△), and propylamine (□) retained per gram of montmorillonite after washing each 2 g sample with 1ℓ of distilled water

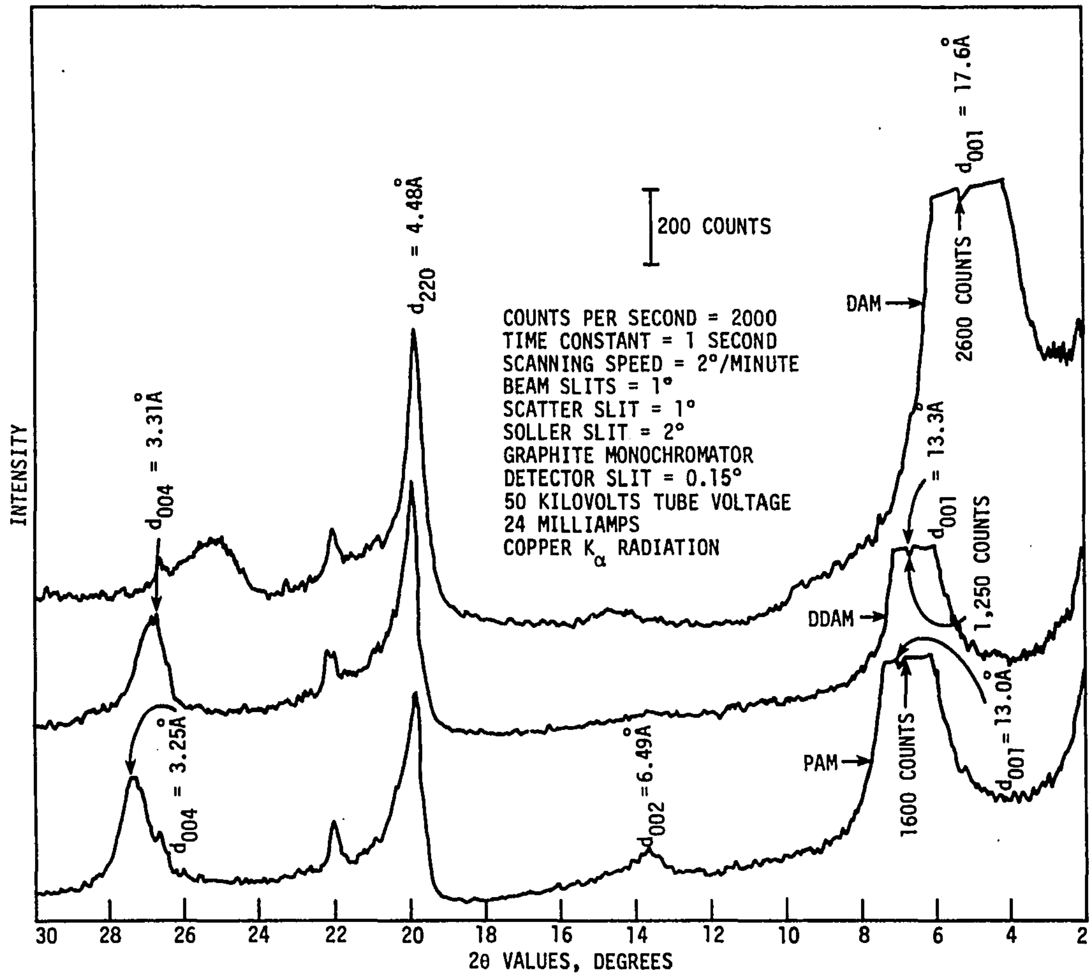


Fig. 19a. X-ray diffraction patterns of dodecylammonium-dodecyldiammonium-, and propylammonium-montmorillonite before washing off excess physically adsorbed amines

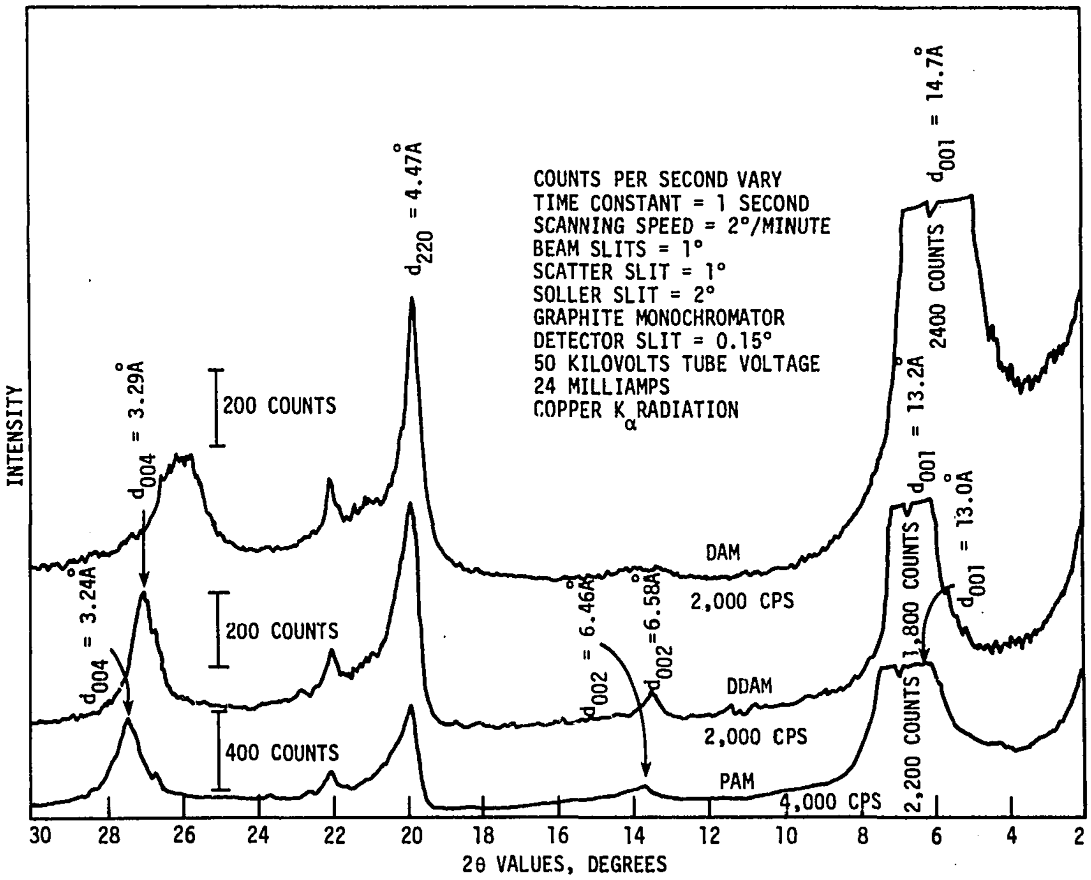


Fig. 19b. X-ray diffraction patterns of dodecylammonium- dodecyldiammonium-, and propylammonium-montmorillonite after washing off excess physically adsorbed amines

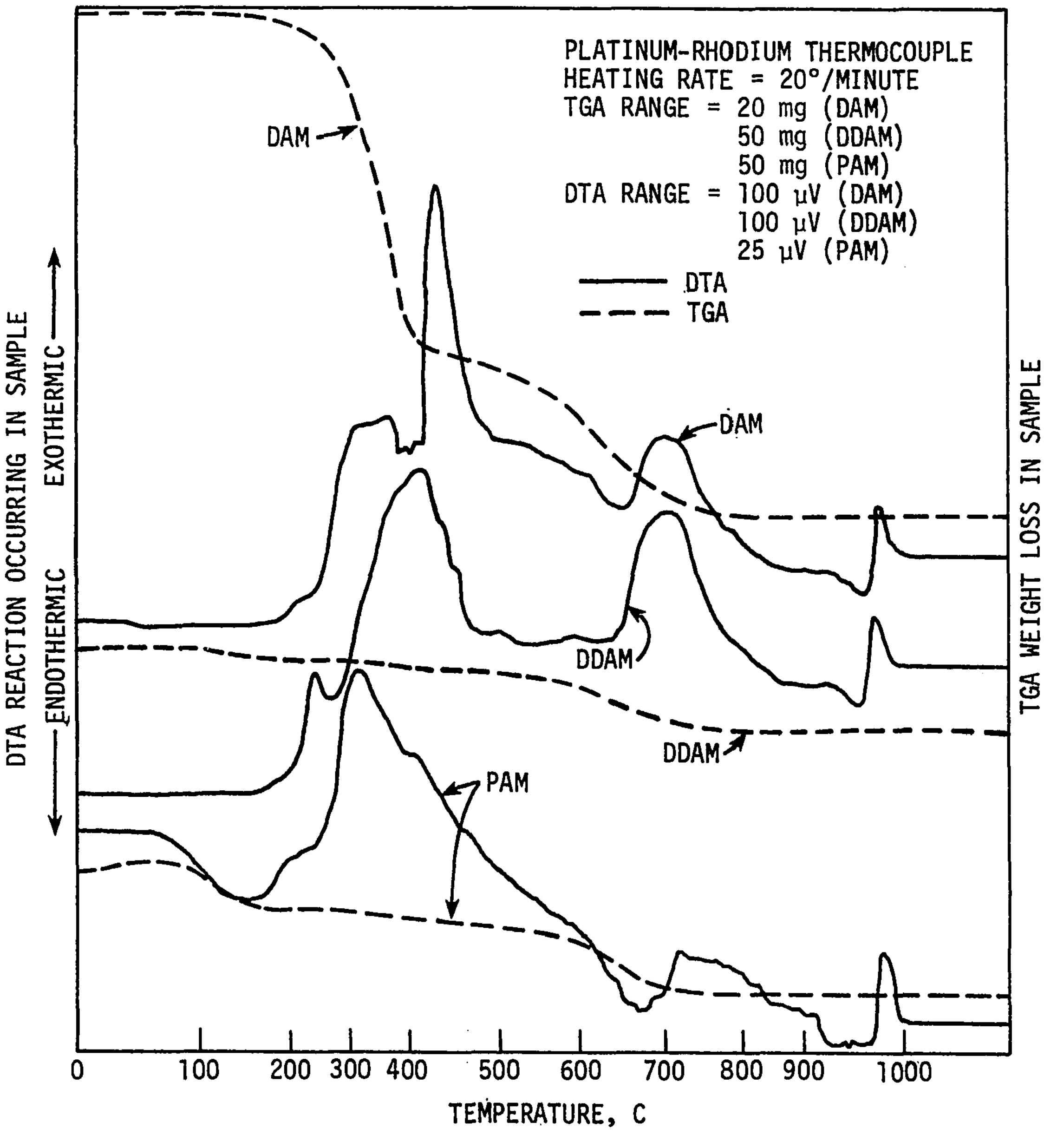


Fig. 20. DTA-TGA curves of dodecylammonium-,dodecyldiammonium-, and propylammonium-montmorillonite after washing off excess physically adsorbed amines

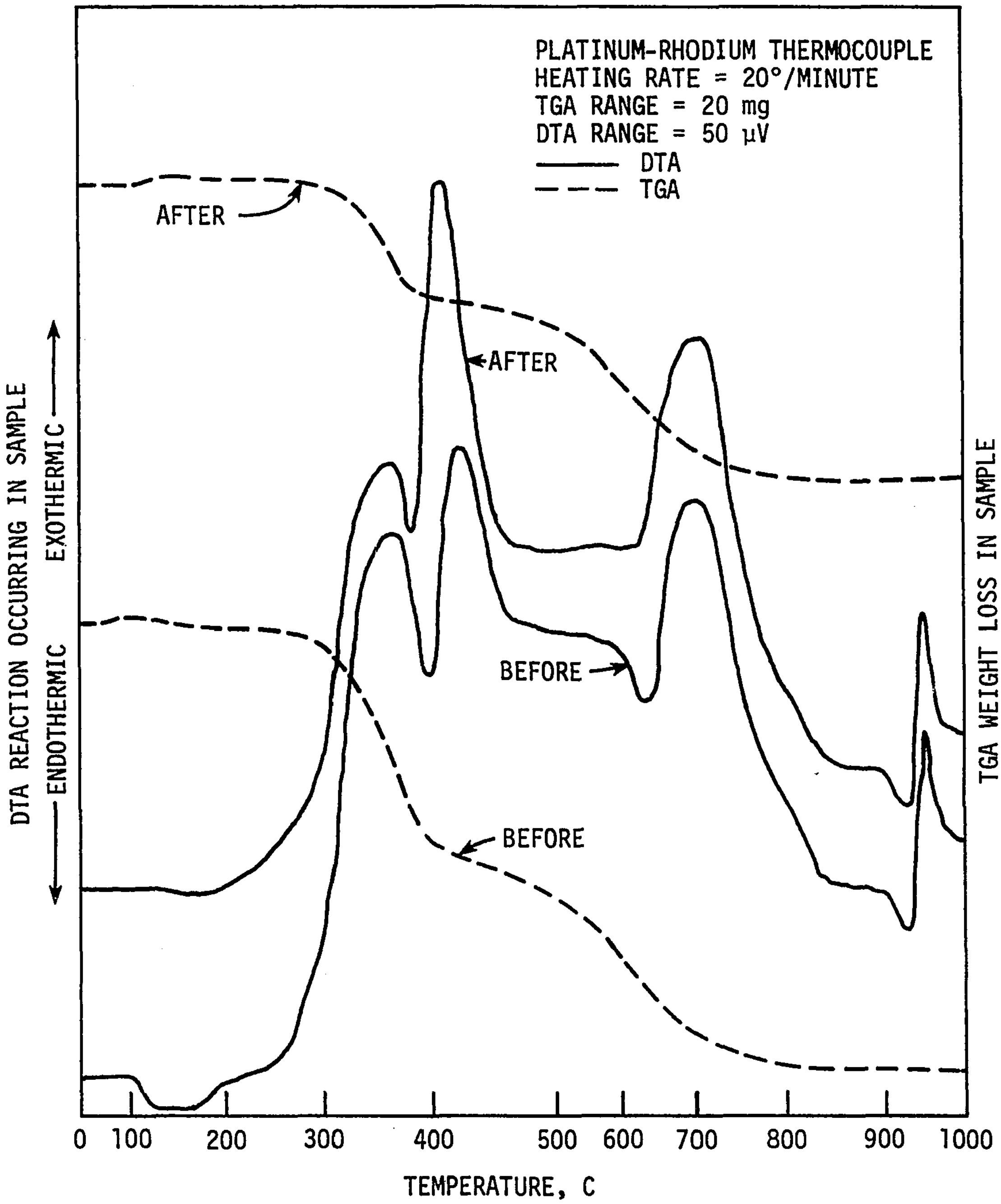
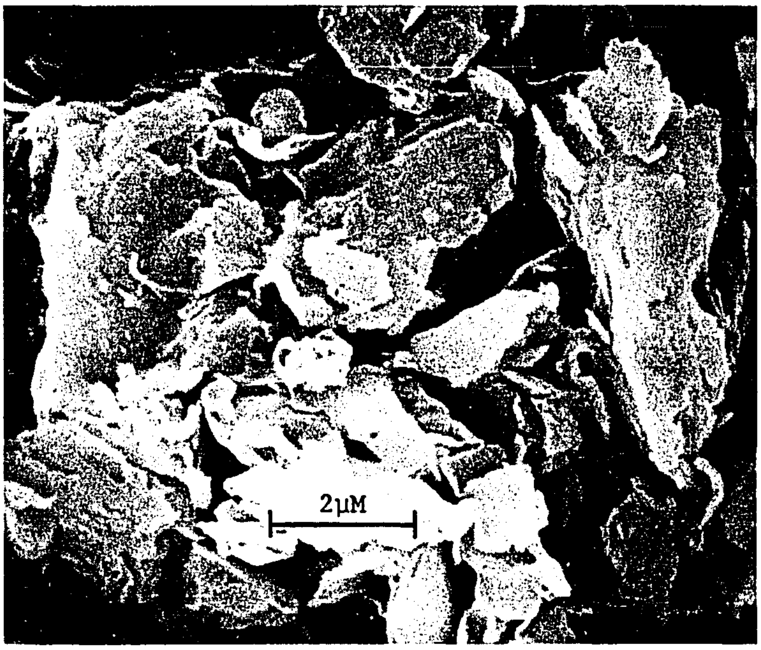
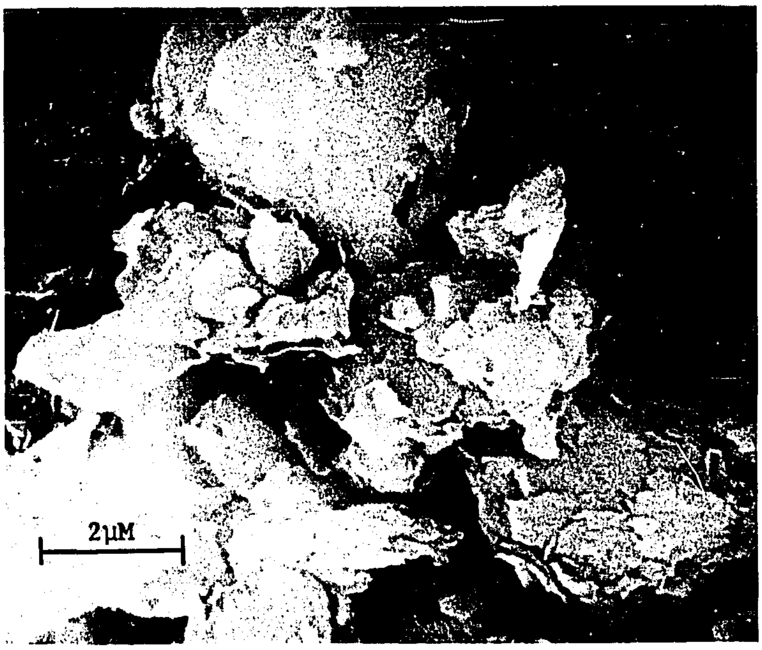


Fig. 21. DTA-TGA curves of dodecylammonium-montmorillonite before and after washing off excess physically adsorbed dodecylamine

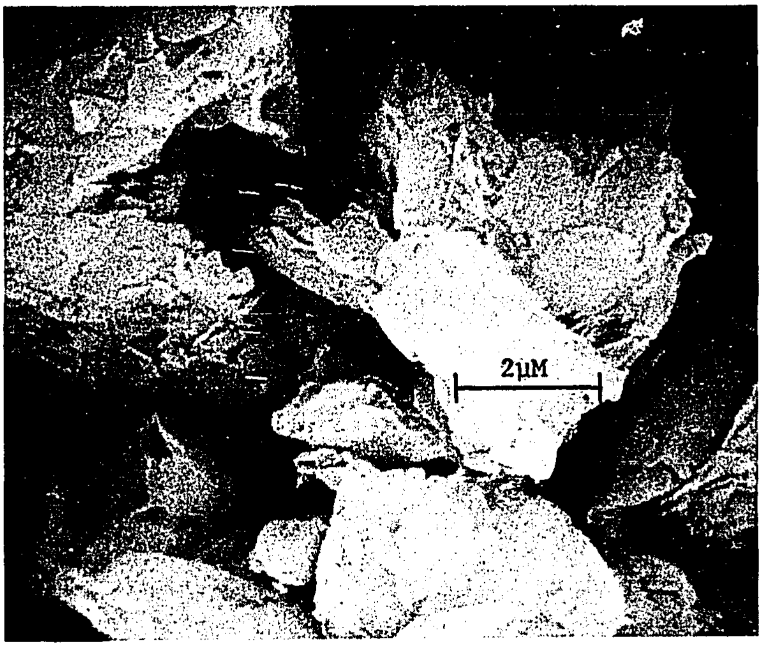


a) dodecylammonium-montmorillonite.



b) dodecyldiammonium-montmorillonite.

Fig. 22. Scanning electron micrographs of dodecylammonium-, dodecyldiammonium-, and propylammonium-montmorillonite; 10,000 X



c) propylammonium-montmorillonite.

Fig. 22. (Continued)

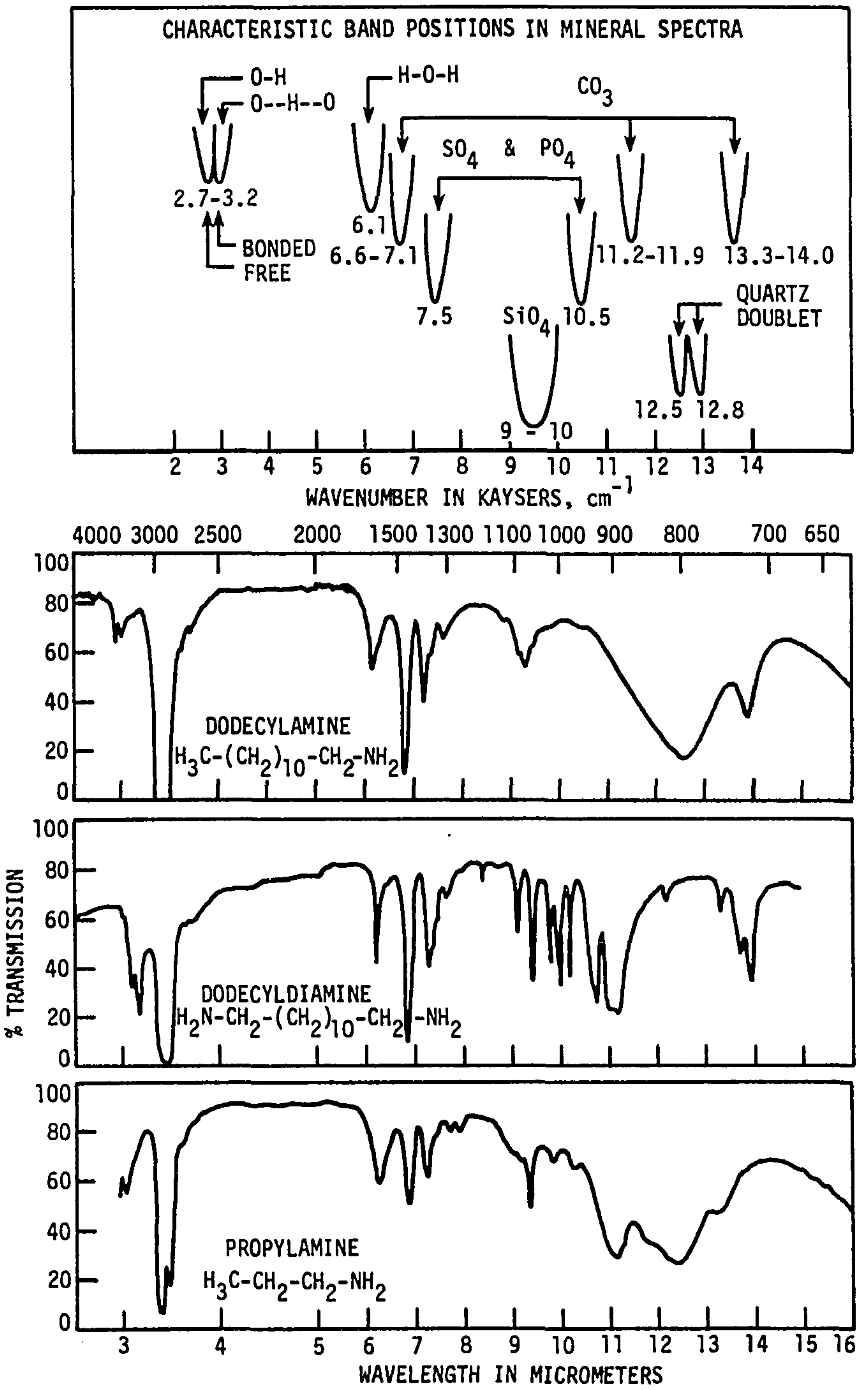


Fig. 23. Infrared absorption spectra of dodecylamine, dodecyldiamine, and propylamine, and characteristic band positions in mineral spectra (107)

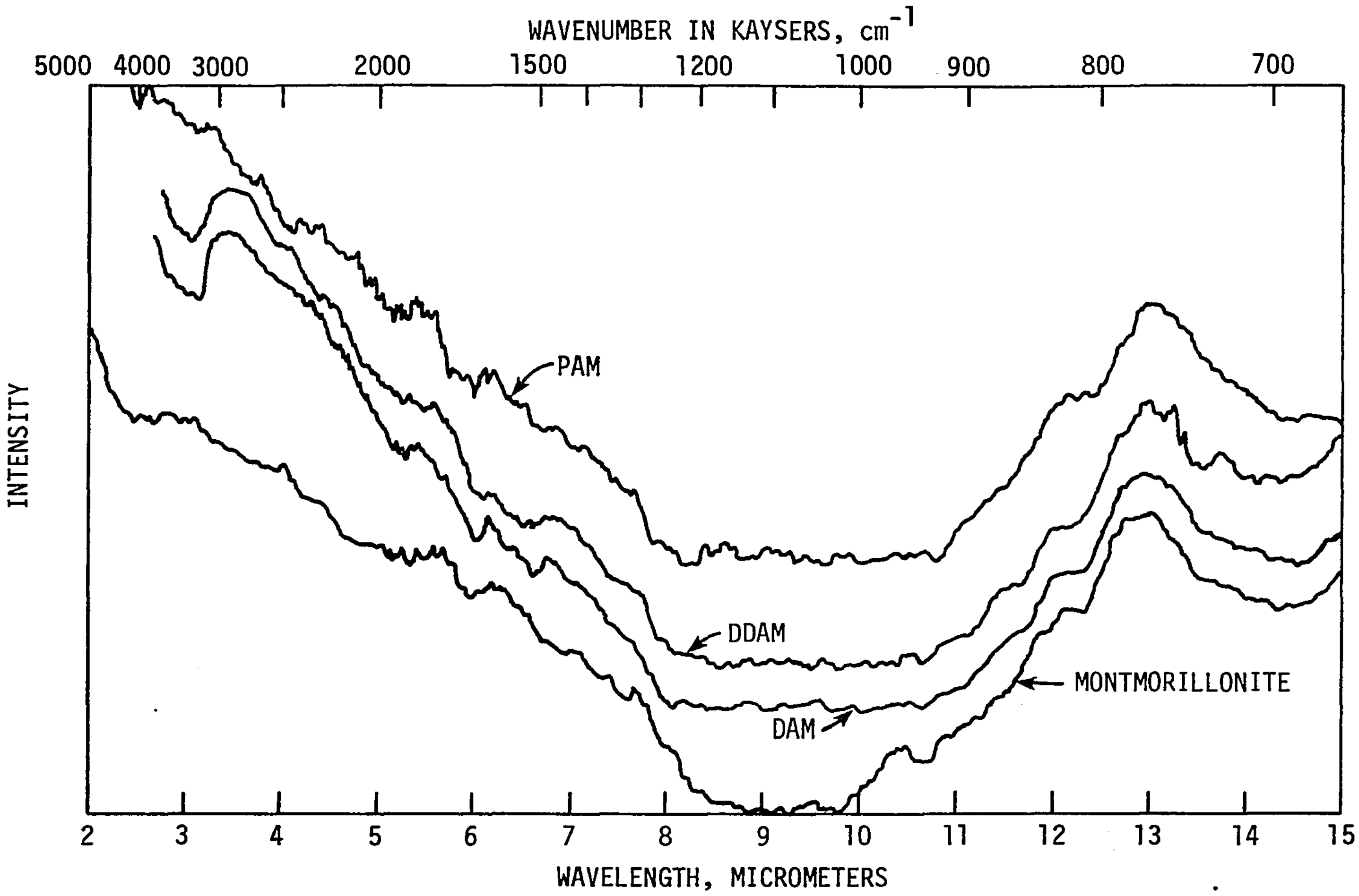


Fig. 24. Infrared absorption spectra of dodecylammonium-, dodecyldiammonium-, and propylammonium-montmorillonite, and untreated montmorillonite

Discussion

The ability of montmorillonite to retain the dodecylammonium (DA), dodecyldiammonium (DDA), and propylammonium (PA) cations is illustrated in Figures 14a, 15a, and 16a, respectively. DA and DDA ions are adsorbed by exchange with sodium ions on the silicate surface when amounts up to the cation-exchange capacity (CEC) of the montmorillonite (approximately 0.94 meq/g) are added. Additional quantities of DA and DDA ions in excess of the CEC of the montmorillonite are adsorbed by a different mechanism, physical adsorption by van der Waals linking of the hydrocarbon chains of the organic cations adsorbed at exchange positions and those of the excess cationic organic molecules. This phenomenon is evident from the decrease in slopes obtained for the regression lines of the data below and above the CEC of the montmorillonite.

PA ions are also adsorbed by exchange with sodium ions on the silicate surface, but were not able to occupy all the exchange sites on the surface. This result is in accordance with those obtained by Servais, et al. (113) when PA ions were adsorbed on sodium-montmorillonite. The fact that approximately only 0.5 meq of PA ions were retained per gram of montmorillonite is due to two major factors. One factor of importance is the relatively high solubility of PA chloride salt in water, 2.8 x 10^6 mg/l (119), as opposed to the much lower solubilities of DA and DDA chloride salts of about 1,500 mg/l, which suggests the PA ions have a high affinity to remain in solution, as opposed to an affinity for adsorption on the surfaces of the montmorillonite by exchange for sodium ions. The second factor of concern is the size of the PA ions, which is similar to that of a molecule of water. Thus, the PA ions and water molecules appear to compete for seats on the silicate surfaces, PA ions for exchange sites and water molecules for hydrating sodium ions on the silicate surface. Additional adsorption of PA ions does not appear to take place when quantities of PA ions are added to the montmorillonite in excess of the CEC.

The data from x-ray diffraction patterns presented in Figures 14b, 15b and 16b provide additional information concerning the adsorption mechanism and orientation within the interlamellar space of the DA, DDA, and PA ions. DA ions form a monolayer within the interlamellar space with increasing concentrations of DA ions up to the CEC with the hydrocarbon chains oriented parallel to the silicate surface. Physical adsorption of the DA ions at concentrations in excess of the CEC results in crowding of the hydrocarbon chains, causing the chains to overlap and to tilt with respect to the silicate surface. When sufficient quantities of DA ions are crowded into the interlamellar space, the hydrocarbon chains orient themselves perpendicularly to the silicate surface.

DDA ions include a positive charge at each end of the hydrocarbon chain and are of the proper length to satisfy two exchange sites on the same silicate surface. A monolayer is formed in the interlamellar space, but sufficient crowding of these ions into the interlamellar space does not occur and the hydrocarbon chains are not forced into an erect position with respect to the silicate surfaces as is the case with DA ions.

Basal spacings in Figures 16b show the PA ions form a monolayer in the interlamellar space with the hydrocarbon chain oriented perpendicularly to the silicate surface. This type of orientation is supported by the d_{001} spacings and the relatively small values for line breadth of the d_{001} peaks at higher concentrations of PA retained by the montmorillonite. This also suggests that PA ions interact differently with the montmorillonite surface than the other two amines and are partly embedded in oxygen-ring cavities associated with cation sites as suggested by Kinter and Diamond (77).

These same adsorption data were fitted to the linear forms of the Langmuir, Freundlich, and Brunauer, Emmett, Teller (BET) adsorption isotherm models:

$$\text{Langmuir model} \quad \frac{1}{q} = \frac{1}{Q^o} + \left(\frac{1}{bQ^o}\right)\frac{1}{C} \qquad (5)$$

where

q = weight of solute adsorbed per unit weight of adsorbent at concentration C

Q^o = weight of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface

b = a constant related to the energy, or net enthalpy, of adsorption

C = measured concentration of solute in solution at equilibrium.

Freundlich model $$\log q = \log K + \frac{1}{n} \log C \qquad (6)$$

where

$\log = \log_{10}$

q = same as in the Langmuir model

K = indicator of adsorption capacity of the adsorbent

$\frac{1}{n}$ = indicator of adsorption intensity

C = same as in the Langmuir model.

BET model $$\frac{C}{(C_s - C)q} = \frac{1}{BQ^o} + \left(\frac{B - 1}{BQ^o}\right) \frac{C}{C_s} \qquad (7)$$

where

C = same as in the Langmuir and Freundlich models

C_s = saturation concentration of the solute

q = same as in the Langmuir and Freundlich models

B = constant expressive of the energy of interaction with the surface

Q^o = same as in the Langmuir model.

The Langmuir adsorption model is valid for only single-layer adsorption and is deduced from either kinetic considerations or the thermodynamics of adsorption. The Freundlich adsorption model is basically empirical and represents a special case of heterogeneous surface energies in which the energy term, b, in the Langmuir model varies as a function of surface coverage, q. The BET adsorption model may also be deduced from kinetic considerations or the thermodynamics of adsorption, and represents isotherms reflecting apparent multilayer adsorption. The data obtained from this isotherm study for DA, DDA, and PA adsorbed on montmorillonite showed a poor fit to the Langmuir and Freundlich adsorption isotherm models as values calculated for the coefficient of determination, r^2, were low. Values of the coefficient of determination for the DA, DDA, and PA adsorption data were 0.18, 0.05, and 0.63 for the Langmuir model, and were 0.74, 0.57, and 0.52 for the Freundlich model. The adsorption data for DA, DDA, and PA plotted for the BET model are shown in Figures 17a, b, and c, respectively. Calculated coefficient of determination values for the adsorption of all three alkylammonium ions are 1.0, or near 1.0, suggesting a good fit of the data to this model for apparent multilayer adsorption.

Within the concentration ranges employed the Langmuir adsorption model should agree quite closely with the BET model. The reason for this discrepancy lies in the fact that data representing low concentrations are emphasized when the Langmuir model is used as written in equation 5. Multiplying all the terms in equation 5 by C gives a Langmuir model in the form:

$$\frac{C}{q} = \frac{C}{Q^o} + \frac{1}{bQ^o} \tag{8}$$

The adsorption data for DA, DDA, and PA plotted for the Langmuir model in this form yield values for the coefficient of determination of 0.76, 1.00, and 0.98, respectively. Since C/q is plotted against C in this model, data representing high concentrations receives the emphasis and the Langmuir adsorption model agrees more closely with the BET model. Such a result is indicative of the experimental error involved with measurement of equilibrium concentrations of the alkylammonium solutions in the low concentration range.

The specific surface of an adsorbent, Σ_s, can be determined by the relationship:

$$\Sigma_s = Q^o N_{Av} \sigma^o / M \qquad (9)$$

where

Σ_s = specific surface of the adsorbent in terms of area per unit weight

Q^o = monolayer coverage value in BET isotherm model

N_{Av} = Avogadro's number, 6.023×10^{23} molecules per mole of solute

σ^o = surface area on adsorbent occupied per molecule of solute.

M = molecular weight of the solute.

Assuming the interlamellar surface area of montmorillonite to be approximately 700 square meters per gram, and using the slopes, $(\frac{B - 1}{BQ^o})$, and intercept values, $\frac{1}{BQ^o}$, from Figures 17a, b, and c, the percent of interlamellar surface area covered by the adsorbed alkylammonium ions can be calculated. Using surface coverage values of 55 Å^2 per molecule for the DA and DDA ions and a value of 11.5 Å^2 per molecule for the PA ion, it was determined that DA ions cover approximately 68 percent of the interlamellar surface area, DDA ions cover about 15 percent of this surface area, the PA ion provides coverage of approximately 5 percent of the interlamellar surface area.

Figure 18 presents the ability of montmorillonite to retain the

DA, DDA, and PA ions after washing each two gram sample of the alkylammonium-montmorillonites in one liter of distilled water. Essentially, only those alkylammonium ions adsorbed by exchange with sodium ions are retained after washing. It is necessary to remove the physically adsorbed alkylammonium ions by washing as these ions take up interlamellar space that can be used to adsorb solutes, but these additional ions are not needed to keep the clay layers separated to permit the organic pollutants to enter the interlamellar space.

Table 5 presents the d_{001} spacings for the three alkylammonium-montmorillonites as found in the literature and as obtained in this study. The variation in basal spacings has been suggested by Weiss (134) to be a result of several factors. A difference in basal spacings can be observed if the samples are swollen in water instead of alcohol before drying in vacuo. Drying the samples at temperatures up to 70° C instead of above 110° C can also affect basal spacing measured. Basal spacings can also be influenced by the degree of grinding to which the samples are subjected.

The effects of the distilled water washing of the alkylammonium-montmorillonites are also noted from the x-ray diffraction patterns in Figures 19a and b, and from DTA-TGA curves in Figures 20 and 21. Figure 21 is especially useful in determining these effects as the magnitude of the two exothermic peaks at 344 and 440 C are different. These peaks represent the dehydrogenation and the initial oxidation of the hydrocarbon chains of the alkylammonium ions. The magnitude and position of these peaks indicate the strength with which the

Table 5. Variation in basal spacings for DAM, DDAM, and PAM

Alkylammonium-Mont.	Method	Basal Spacing, Å	Reference
Dodecylammonium	wa[a]	15.1	this study
	wo[b]	14.7	
	wow[c]	16.1	
	no	17.8	(70)
	w, wag[d]	16.4, 38.4	(29)
	w, wag	17.7, 34.0	
	w, wag	16.1, 35.0	
	w, wag	18.2, 37.7	
	eo[e]	14.6	(11)
	m[f]	16.3	(121)
	mw[g]	20.0	
	wa	15.4	(134)
	wo	14.3	
Dodecyldiammonium	wo	13.2	this study
	wow	13.2	
	eo	13.4	(11)
Propylammonium	wo	13.1	this study
	ww	13.2	
	wa	13.4	(55)
	eo	13.1	(11)
	b[h]	12.9	(79)

---

[a] wa, excess washed off with water and sample air dried.

[b] wo, excess washed off with water and sample dried at 60 C.

[c] wow, sample saturated with water after wo treatment.

[d] wag, sample saturated with ethylene glycol after wa treatment.

[e] eo, excess washed off with ethanol and sample dried at 60 C.

[f] m, excess washed off with methanol.

[g] mw, sample saturated with water after m treatment.

[h] b, adsorbed on montmorillonite from benzene solution.

alkylammonium ions are held in the interlamellar space. The magnitude of the peaks decreases after washing, showing that the alkylammonium ions attached by physical adsorption have been removed. The endothermic peak at 740 C for dehydroxylation in Figure 12 is also affected by the adsorption of alkylammonium ions. This is due to the fact that dehydrogenation of the hydrocarbon chains takes place in the exothermic peaks at 344 and 440 C, leaving a coating of carbon between the silicate layers that does not burn off until dehydroxylation occurs. The dehydroxylation peak is shifted to a lower temperature, 644 versus 740 C, followed by an exothermic peak representing the oxidation of the carbon coating as suggested by Allaway (2). Jordan (71) and Byrne (29) also observed similar DTA-TGA results for dodecylammonium-bentonite.

Figure 22 presents the scanning electron micrographs, at a magnification of 10,000 X, of the three alkylammonium-montmorillonites. The effect on the morphology of the montmorillonite by adsorption of these alkylammonium cations on sodium-montmorillonite can be determined from these micrographs. It has been discussed earlier that sodium-montmorillonite is rendered somewhat organophilic (hydrophobic) by the exchange of alkylammonium cations for sodium ions, and the extent of organophilicity increases with extent of this exchange and with increasing hydrocarbon chain length of the alkylammonium cations. The sheets of alkylammonium-montmorillonites exhibit a tendency to curl as they become more organophilic. The electron micrograph of dodecylammonium-montmorillonite shows evidence of this curling.

Jernigan and McAtee (69) suggested a possibility for this morphology change in montmorillonites treated with alkylammonium cations. Results from their work indicate the curling of the montmorillonite sheets occurs in aqueous solution when exchange of the organic cations for sodium ions occurs since the montmorillonite particles tend to aggregate with an overlapping of sheets in order to reduce the surface area exposed to the solvent. The results in this study for the preparation of DAM follow this same pattern as flocculation of the suspension was observed when sodium-montmorillonite was immersed in the dodecylammonium chloride solution.

The adsorption bands displayed by the primary amine functional group are presented in Figure 23 (107). Characteristic absorption bands occur at 3 micrometers (3335 cm^{-1}) for the NH_2 nitrogen-hydrogen stretch, 6.2 micrometers (1615 cm^{-1}) for the NH_2 deformation, and between 11 and 13 micrometers (910-770 cm^{-1}) for the NH_2 wag (oscillation).

The absorption bands in Figure 24 for the amines at 6.2 and between 11 and 13 micrometers are masked by montmorillonite absorption bands occurring in these regions. The presence of the amines in the interlamellar space of the montmorillonite is confirmed by the absorption bands in Figure 24 that occur at 3 micrometers (3335 cm^{-1}) for DAM and DDAM. Although montmorillonite displays an absorption band in this region, drying of the samples minimizes this montmorillonite absorption band and the amine absorption band is detected.

The absorption band in Figure 24 for PAM at 2.5 micrometers (4000 cm^{-1}) may be the result of two factors. One, it is possible the montmorillonite is masking the propylamine adsorption band and the band displayed at 2.5 micrometers may be adsorbed water. Secondly, this band may be the propylamine band, but its location is shifted because the propylamine is interacting differently than the other two amines with the montmorillonite surface and is partly embedded in oxygen-ring cavities associated with cation sites as was postulated previously.

EXPERIMENTAL PHASE B

Phase A involved purification of Wyoming bentonite to obtain the montmorillonite fraction, and subsequent treatment of the montmorillonite with the hydrochloride salts of three n-aliphatic amines to open the interlamellar spaces of the clay. Besides expanding the clay laminae adsorption of the amines provides surfaces in the interlamellar space of both a hydrophilic and hydrophobic (organophilic) nature.

Experimental Phase B is an evaluation of the adsorption of eleven organic materials commonly found in water and wastewater on the expanded montmorillonite. Isotherms were performed at an organic concentration in distilled water of 100 milligrams per liter for all eleven organics and at an organic concentration of 1,000 milligrams per liter for six of the more soluble organic materials. X-ray diffraction studies were also completed of clay saturated with solutions of the eleven organic compounds in distilled water at concentrations from 0 percent to 100 percent, by weight, to determine the effects of adsorption of the organics on the basal spacings of the amine treated montmorillonites and the untreated montmorillonite.

Isotherms of Eleven Organic Compounds Adsorbed on Alkylammonium-Montmorillonites and Montmorillonite

The selection of organic materials to be studied, Table 6, was difficult because of the many criteria available upon which to base a decision. Seven of the eleven compounds selected were among the one

Table 6. Eleven organic compounds adsorbed on expanded montmorillonite

Organic Compound	Chemical Class (1)	Molecular Formula (131)	Solubility in water @ 20 C, mg/l (131)	Boiling Point, C (131)	Manufacturer Source
Acetaldehyde[a,b]	Aldehyde	CH_3CHO	∞	20.2	Eastman Kodak Company
Acetone[a,b,c]	Ketone	CH_3COCH_3	∞	56.2	Burdick & Jackson Labs
Benzene[a,d,b]	Unsubstituted Aromatic	C_6H_6	1,780	80.1	Burdick & Jackson Labs
Butanol	Alcohol	$CH_3(CH_2)_3OH$	77,000	117.7	Fisher Scientific Company
Chloroform[a,d,c]	Alkane	$CHCl_3$	8,000	+62	Fisher Scientific Company
Dimethylphthalate[a,d]	Ester	$C_6H_4(COOCH_3)_2$	5,000	282	Aldrich Chemical Company
Hexanol	Alcohol	$CH_3(CH_2)_5OH$	5,900	158	Eastman Kodak Company
Nitrobenzene[a,d]	Nitrosubstituted Aromatic	$C_6H_5NO_2$	1,900	211	Fisher Scientific Company
Octanol	Alcohol	$CH_3(CH_2)_7OH$	300	195	Eastman Kodak Company
Phenol[d]	Phenolic Aromatic	C_6H_5OH	82,000[e]	182	Aldrich Chemical Company
Toluene[a,d,c]	Arylalkane Aromatic	$C_6H_5CH_3$	515	110.8	Burdick & Jackson Labs

[a] Appear in the list of 154 compounds identified in drinking water (1).

[b] Appears in the list of compounds thought to be formed during biological phase of wastewater treatment (1).

[c] Appears in the list of compounds positively identified in sewage treatment plant effluents (1).

[d] *Appears in the list of 65 toxic pollutants (50, 75) and 129 EPA priority pollutants (75).*

[e] Measured at 15 C.

hundred fifty-four organic compounds identified in the drinking water supplies of communities on the Ohio, Potomac, and Mississippi Rivers (Appendix A (1)). Six of the eleven appear in the list of sixty-five toxic pollutants (Appendix A (50, 75)) that resulted from a June 7, 1976 Consent Decree in the case of the Natural Resources Defense Council, Inc. versus Train as the representative of EPA. These same six compounds are also included in an EPA list of one hundred twenty-nine priority pollutants (Appendix A (75)).

In terms of wastewater treatment, three of the eleven are compounds which were suspected of being formed during the biological phase of wastewater treatment (Appendix A (1)). Three of the eleven were compounds positively identified in sewage treatment plant effluents (Appendix A (1)).

The chemical class of each of the eleven organic compounds selected was also important as it was desirable to study the ability of the amine treated clays to interact with various organic functional groups. Table 6 also shows the different chemical classes to which the eleven compounds belong.

It should be noted that the three alcohols studied do not appear in any of the lists discussed above, but were selected to serve as a check for experimental procedures as a few recent studies (120, 121) have examined the adsorption of these alcohols on dodecylammonium-montmorillonite.

One last set of criteria of concern was the solubilities of the organic compounds in water, and the ability to analyze for these compounds using gas chromatography. It was necessary to pick compounds fairly soluble in water so significant amounts would not be lost in the vapor phase during the isotherm study. On the other hand, the compounds had to be relatively volatile so they could be easily detected using gas chromatography techniques. Solubilities of the eleven compounds in water are also given in Table 6.

Procedures

Two-liter, stock solutions of each organic compound were prepared in distilled water at concentrations of 100 milligrams per liter or 1,000 milligrams per liter prior to the start of individual adsorption isotherm studies. A small portion of the stock solution was diluted with distilled water to provide the standard series of 100, 50, and 25 milligrams per liter or 1,000, 500, and 250 milligrams per liter necessary for standardizing the gas chromatograph.

Twelve, 250-milliliter conical flasks were used in performing each isotherm. Samples of 100 milliliters of a stock solution were pipetted into each conical flask. Quantities of dodecylammonium-montmorillonite (DAM), dodecyldiammonium-montmorillonite (DDAM), propylammonium-montmorillonite (PAM), and untreated montmorillonite (Mont.) were placed in the flasks according to the schedule outlined in Table 7. The quantity of desiccated clay was weighed out and the weights listed in Table 7 indicate not only the montmorillonite but also the weight of the amines adsorbed on the clay. The flasks were tightly stoppered and placed in a mechanical shaker (Water-Bath-Shaker by Eberbach Corporation, Ann Arbor,

Table 7. Quantities of clay added to each flask in the isotherm study

Flask Number	DAM mg	DDAM mg	PAM mg	Mont. mg
1	100			
2	200			
3	300			
4		100		
5		200		
6		300		
7			100	
8			200	
9			300	
10				100
11				300
12 Control Sample (no clay)				

Michigan) is a constant temperature room at 20 C for forty-eight hours.

The clay was seperated from the liquid in a 47-millimeter diameter stainless steel pressure filter funnel (Gelman Instrument Company, Ann Arbor, Michigan) with GA-6, 0.45 micrometer Metrical R , membrane filters (Gelman Sciences, Inc., Ann Arbor, Michigan). Nitrogen gas was used to provide the pressure, with pressures utilized varying from sample to sample. Generally, the dodecylammonium-montmorillonites (DAM) required pressures slightly in excess of atmospheric pressure, the dodecyldiammonium-montmorillonites (DDAM) and proplyammonium-montmorillonites (PAM) required 30 to 50 pounds per square inch of pressure, and the untreated montmorillonite (Mont.) required a pressure of approximately 100 pounds per square inch.

Liquid samples of the filter effluent were collected in 17 x 60 millimeter, 2-dram, glass vials (Kimble, Division of Owens-Illinois), sealed with screw caps with a hole in the top, and lined with 13-millimeter diameter teflon/rubber septa (Alltech Associates, Deerfield, Illinois). The teflon side of the septa was in contact with the sample. The hole in the top of the screw cap made it possible to insert the needle of a 10 microliter graduated syringe (Hamilton Co., Reno, Nevada) through the teflon/rubber septum for extraction of two microliter samples for analysis by gas chromatography.

The teflon/rubber septa were used because gas chromatography results obtained with liquid samples stored in chemical oxygen demand vials from Hach Chemical Company showed evidence of the organics being adsorbed on the inside coating of the caps.

X-ray diffraction patterns were run on the clay collected on the Gelman filter paper immediately after filtration and after twenty-four hours of air-drying. The filter effluent samples were analyzed on a gas chromatograph (Hewlett-Packard, Model 5730-A). Column packings and experimental conditions used to analyze for each of the eleven organic compounds are listed in Table 8. Samples of the gas in the space above the liquid in the control flask were analyzed by gas chromatography to determine if significant quantities of the organics had permeated into the gas phase. The liquid portion of the control was analyzed before and after filtration in the Gelman filter apparatus to confirm that filtration of the samples did not alter the organic content of the liquid phase.

Table 8. Gas chromatograph conditions used to analyze for the eleven organic compounds

	Temperatures, C							
Organic Compound	Injection	Oven	Detector	Detector	Column Packing	Range	Attenuation	Detention Time
Acetaldehyde	150	80	250	Flame Ionization	0.2% Carbowax 1500 on Carbopack C	10	16	15 sec.
	200	80	250			100	16	15 sec.
Acetone	200	90	250	"	0.2% Carbowax 1500 on Carbopack C	10	8	30 sec.
	200	90	250			10	128	30 sec.
Benzene	200	130	250	"	Supelco 1-1827 and 0.2% Carbowax 1500 on 80/100	10	4	1 min.
Butanol	200	130	250	"	"	10	4	1 min.
Chloroform	200	115	250[a]	"	"	1	2	2 min.
	150	115	250	"		10	8	30 sec.
Dimethylphthalate	250	180	300	"	1.5% SP-2250/1.95% SP-2401	10	8	1 min.
	250	180	300			100	8	30 sec.
Hexanol	250	180	300	"	Tenax, 8100 Mesh	10	4	2 min.
	200	180	250[b]			100	4	1 min.
Nitrobenzene	200	100	250	"	1.5% SP-2250/ 1.95% SP-2401	10	8	2 min.
Octanol	250	200	300	"	Tenax, 8100 Mesh	10	4	2 min.
Phenol	200	200	250	"	Tenax GC	10	4	2 min.
	200	200	250			10	64	2 min.
Toluene	200	160	250	"	0.2% Carbowax 1500 on Carbopack C	10	4	1 min.

[a] 4 μl sample injected.

[b] 1.6 μl sample injected.

Results

Table 9 presents the isotherm results for the amounts of each of the eleven organic compounds adsorbed per gram of dodecylammonium-montmorillonite (DAM), dodecyldiammonium-montmorillonite (DDAM), propylammonium-montmorillonite (PAM), and untreated montmorillonite (Mont.) from an initial organic solution concentration of 100 milligrams per liter. Also listed in Table 9 are some representative basal spacings, d_{001} values, and the line breadths, B_0 values, obtained from x-ray diffraction patterns of the clays collected on the Gelman filter paper before and after drying the samples.

Table 10 presents the same parameters as does Table 9, but the results are for six of the eleven compounds reacted with the clays at an initial organic solution concentration of 1,000 milligrams per liter.

Figures 25a, b, c and d, and Figures 26a, b, c and d show the ability of the clays to adsorb the various organic compounds based on the solubility of the eleven compounds in water at 20 C. Figures 25a, b, c and d present the data from Table 9 and Figures 26a, b, c and d present the data from Table 10. Numbers on the figures identify the various organic compounds as they are listed in Tables 9 and 10.

Discussion

Figures 25a, b, c and d, and Figures 26a, b, c and d, show a slight tendency for the less soluble organic compounds to be more readily adsorbed on the clays. Equilibrium concentrations shown in these figures are adjusted for solute lost in the vapor phase and differences between the initial concentration and equilibrium concentrations reflect only adsorption by the clays.

Table 9. Isotherm results for the eleven organic compounds at an initial organic solution concentration of 100 milligrams per liter

Clay	Clay mg	Equilibrium Concentration mg/l	Ads/DAM mg/g	Ads/DDAM mg/g	Ads/PAM mg/g	Ads/Mont. mg/g	d_{001}, Å^a Wet	Dry	B_o, Degrees Wet	Dry
Acetaldehyde [1]										
DAM	100	91 ± 16	9.0							
	200	82 ± 5	9.0				16.4	14.3	1.2	1.5
	300	79 ± 2	7.0							
DDAM	100	89 ± 5		11						
	200	86 ± 2		7.0			13.3	12.7	0.55	0.55
	300	71 ± 2		10						
PAM	100	84 ± 9			16					
	200	64 ± 5			18		13.4	12.9	1.0	0.9
	300	52 ± 7			12					
Mont.	100	88 ± 11				12	∞	13.5	-	2.1
	300	100 ± 4				0				
Control	-	100 ± 0								
Acetone [2]										
DAM	100	98 ± 1	0							
	200	98 ± 4	0				16.7	14.1	1.1	1.5
	300	96 ± 1	0							
DDAM	100	99 ± 0		0						
	200	96 ± 6		0			13.0	12.7	0.5	0.6
	300	99 ± 2		0						
PAM	100	93 ± 1			7.0					
	200	92 ± 3			4.0		13.0	12.7	1.0	0.6
	300	88 ± 3			4.0					
Mont.	100	97 ± 2				0				
	300	97 ± 1				0	∞	12.6	-	2.5
Control	-	98 ± 3								
Benzene [3]										
DAM	100	40 ± 1	8.0							

	200	41 ± 5	4.0				16.4	13.8	1.2	1.5
	300	40 ± 3	3.0							
DDAM	100	46 ± 7		2.0						
	200	41 ± 5		4.0			13.1	12.3	0.6	0.6
	300	44 ± 1		1.0						
PAM	100	33 ± 2			15					
	200	29 ± 0			10		13.4	12.5	1.5	1.2
	300	28 ± 3			7.0					
Mont.	100	29 ± 3				19				
	300	20 ± 1				9.0	∞	13.2	-	1.7
Control	-	48 ± 1								
<u>Butanol</u> [4]										
DAM	100	99 ± 4	1.0							
	200	96 ± 4	2.0				-	14.2	-	1.9
	300	95 ± 4	1.7							
DDAM	100	98 ± 8		2.0						
	200	96 ± 2		2.0			-	12.6	-	0.45
	300	93 ± 1		2.3						
PAM	100	90 ± 7			10					
	200	84 ± 7			8.0		-	12.6	-	0.8
	300	83 ± 1			6.0					
Mont.	100	90 ± 3				10				
	300	70 ± 1				10	-	12.1	-	1.8
Control	-	100 ± 6								
<u>Chloroform</u> [5]										
DAM	100	50 ± 0	0							
	200	52 ± 1	0				16.9	14.2	1.1	1.5
	300	51 ± 4	0							
DDAM	100	46 ± 1		4.0						
	200	47 ± 0		2.0			13.4	13.1	0.6	0.5
	300	45 ± 1		2.0						
PAM	100	34 ± 0			16					
	200	36 ± 0			7.0		13.4	12.7	1.2	0.7
	300	34 ± 1			5.0					

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[a] Basal spacing in angstroms.

Table 9. (continued)

							d_{001}, Å^a		B_o, Degrees	
Clay	Clay mg	Equilibrium Concentration mg/l	Ads/DAM mg/g	Ads/DDAM mg/g	Ads/PAM mg/g	Ads/Mont. mg/g	Wet	Dry	Wet	Dry
Mont.	100	34 ± 1				16				
	300	30 ± 1				5.0	∞	13.2	-	2.2
Control	-	50 ± 1								
Dimethylphthalate [6]										
DAM	100	75 ± 3	25							
	200	65 ± 0	18				17.0	14.5	1.1	1.6
	300	57 ± 6	14							
DDAM	100	96 ± 5		4.0						
	200	97 ± 6		2.0			13.2	13.0	0.6	0.5
	300	93 ± 2		2.0						
PAM	100	57 ± 2			43					
	200	48 ± 0			26		13.4	12.7	1.2	0.75
	300	57 ± 2			14					
Mont.	100	54 ± 0				46	-	13.4	-	1.6
	300	53 ± 3				16	∞	-	-	-
Control	-	100 ± 4								
Hexanol [7]										
DAM	100	99 ± 2	0							
	200	93 ± 2	3.0				-	14.7	-	1.6
	300	96 ± 2	1.0							
DDAM	100	91 ± 1		8.0						
	200	90 ± 2		5.0			-	12.8	-	0.55
	300	91 ± 5		3.0						
PAM	100	83 ± 3			16					
	200	74 ± 3			13		-	12.4	-	0.8
	300	72 ± 3			9.0					
Mont.	100	90 ± 1				9.0				
	300	84 ± 2				5.0	-	12.6	-	1.9
Control	-	99 ± 2								

Nitrobenzene [8]										
DAM	100	72 ± 5	6.0							
	200	72 ± 0	3.0				16.7	13.9	1.1	1.5
	300	70 ± 5	3.0							
DDAM	100	67 ± 0		11						
	200	67 ± 2		6.0			13.1	12.6	0.55	0.6
	300	63 ± 6		5.0						
PAM	100	51 ± 4			27					
	200	42 ± 4			18		13.2	12.3	1.3	0.9
	300	38 ± 2			13					
Mont.	100	47 ± 0				31				
	300	32 ± 4				15	∞	12.0	-	1.9
Control	-	78 ± 2								
Octanol [9]										
DAM	100	74 ± 3	16							
	200	69 ± 3	11				-	15.0	-	1.5
	300	61 ± 4	10							
DDAM	100	80 ± 2		10						
	200	84 ± 2		3.0			-	12.6	-	0.5
	300	74 ± 2		5.0						
PAM	100	64 ± 2			26					
	200	43 ± 2			24		-	12.8	-	1.3
	300	45 ± 3			15					
Mont.	100	66 ± 1				24				
	300	67 ± 2				8.0	-	12.8	-	2.2
Control	-	90 ± 3								
Phenol [10]										
DAM	100	95 ± 1	5.0							
	200	98 ± 1	1.0				-	14.5	-	1.5
	300	95 ± 5	2.0							
DDAM	100	100 ± 1		0						
	200	98 ± 1		1.0			-	12.9	-	0.5
	300	98 ± 0		1.0						
PAM	100	93 ± 1			7.0					
	200	88 ± 4			6.0		-	12.9	-	0.5
	300	94 ± 1			2.0					

Table 9. (continued)

Clay	Clay mg	Equilibrium Concentration mg/l	Ads/DAM mg/g	Ads/DDAM mg/g	Ads/PAM mg/g	Ads/Mont. mg/g	d_{001}, Å^a		B_o, Degrees	
							Wet	Dry	Wet	Dry
Mont.	100	88 ± 5				12				
	300	94 ± 2				2.0	-	11.3	-	1.5
Control	-	100 ± 1								
<u>Toluene</u>	[11]									
DAM	100	22 ± 2	4.0							
	200	20 ± 1	3.0				16.2	14.2	1.3	1.5
	300	26 ± 1	0							
DDAM	100	22 ± 2		4.0						
	200	25 ± 1		1.0			13.4	12.6	0.5	0.6
	300	28 ± 1		0						
PAM	100	13 ± 0			13					
	200	8 ± 1			9.0		13.4	12.2	1.6	0.8
	300	9 ± 0			6.0					
Mont.	100	16 ± 1				10				
	300	7 ± 1				6.0	∞	11.8	-	1.7
Control	-	26 ± 3								

Table 10. Isotherm results for six of the eleven organic compounds at an initial organic solution concentration of 1,000 milligrams per liter

Clay	Clay mg	Equilibrium Concentration mg/l	Ads/DAM mg/g	Ads/DDAM mg/g	Ads/PAM mg/g	Ads/Mont. mg/g	d_{001}, Å^{a} Wet	d_{001}, Å^{a} Dry	B_o, Degrees Wet	B_o, Degrees Dry
<u>Acetaldehyde</u> [1]										
DAM	100	1,000 ± 13	0							
	200	988 ± 7	0				16.1	14.6	1.5	1.65
	300	942 ± 1	15							
DDAM	100	988 ± 23		0						
	200	977 ± 11		6.0			13.4	12.8	0.55	0.7
	300	942 ± 13		15						
PAM	100	965 ± 7			23					
	200	919 ± 35			35		13.6	12.7	0.9	0.9
	300	826 ± 11			54					
Mont.	100	965 ± 7				23				
	300	953 ± 11				12	∞	13.0	-	2.1
Control	-	988 ± 11								
<u>Acetone</u> [2]										
DAM	100	767 ± 46	210							
	200	814 ± 41	82				16.5	14.2	1.2	1.5
	300	802 ± 7	58							
DDAM	100	1,023 ± 66		0						
	200	1,035 ± 53		0			13.3	12.8	0.6	0.5
	300	1,012 ± 37		0						
PAM	100	1,058 ± 43			0					
	200	965 ± 40			6.0		13.0	12.7	0.85	0.7
	300	1,000 ± 44			0					
Mont.	100	977 ± 33				0				
	300	977 ± 33				0	∞	12.6	-	1.8
Control	-	977 ± 20								
<u>Chloroform</u> [5]										
DAM	100	542 ± 23	14							
	200	514 ± 14	21				17.0	14.7	0.8	1.3
	300	486 ± 5	23							

DDAM	100	514 ± 9		42						
	200	500 ± 19		28			13.1	12.8	0.5	0.55
	300	472 ± 14		28						
PAM	100	458 ± 19			98					
	200	403 ± 11			77		13.4	13.5	1.3	1.0
	300	396 ± 28			53					
Mont.	100	375 ± 23				181				
	300	361 ± 15				65	∞	14.0	-	1.6
Control	-	556 ± 28								
<u>Dimethylphthalate</u> [6]										
DAM	100	829 ± 29	171							
	200	707 ± 11	147				17.8	16.8	0.6	0.6
	300	695 ± 23	102							
DDAM	100	1,000 ± 7		0						
	200	951 ± 24		25			13.3	12.7	0.55	0.55
	300	824 ± 35		49						
PAM	100	744 ± 18			256					
	200	634 ± 13			183		17.5	16.8	0.55	0.9
	300	489 ± 6			170					
Mont.	100	732 ± 17				268				
	300	409 ± 0				197	17.8	15.1	0.65	1.25
Control	-	927 ± 18								
<u>Hexanol</u> [7]										
DAM	100	1,000 ± 12	0							
	200	966 ± 36	17				16.4	14.1	1.4	1.6
	300	943 ± 45	19							
DDAM	100	1,000 ± 12		0						
	200	966 ± 26		17			12.8	12.6	0.75	0.75
	300	955 ± 26		15						
PAM	100	943 ± 63			57					
	200	932 ± 29			34		13.4	12.6	0.9	0.8
	300	898 ± 99			34					

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[a] Basal spacing in angstroms.

Table 10. (continued)

Clay	Clay mg	Equilibrium Concentration mg/l	Ads/DAM mg/g	Ads/DDAM mg/g	Ads/PAM mg/g	Ads/Mont. mg/g	d_{001}, Å[a]		B_o, Degrees	
							Wet	Dry	Wet	Dry
Mont.	100	878 ± 38				122				
	300	875 ± 41				42	∞	12.6	-	1.6
Control	-	1,000 ± 33								
Phenol [10]										
DAM	100	974 ± 35	0							
	200	974 ± 15	0				16.7	15.0	1.2	1.6
	300	961 ± 20	0							
DDAM	100	921 ± 40		40						
	200	921 ± 8		20			13.4	12.8	0.6	0.75
	300	934 ± 43		9.0						
PAM	100	895 ± 23			66					
	200	895 ± 15			33		13.4	12.5	1.25	0.8
	300	921 ± 15			13					
Mont.	100	763 ± 20				198				
	300	882 ± 13				26	∞	12.5	-	2.2
Control	-	961 ± 23								

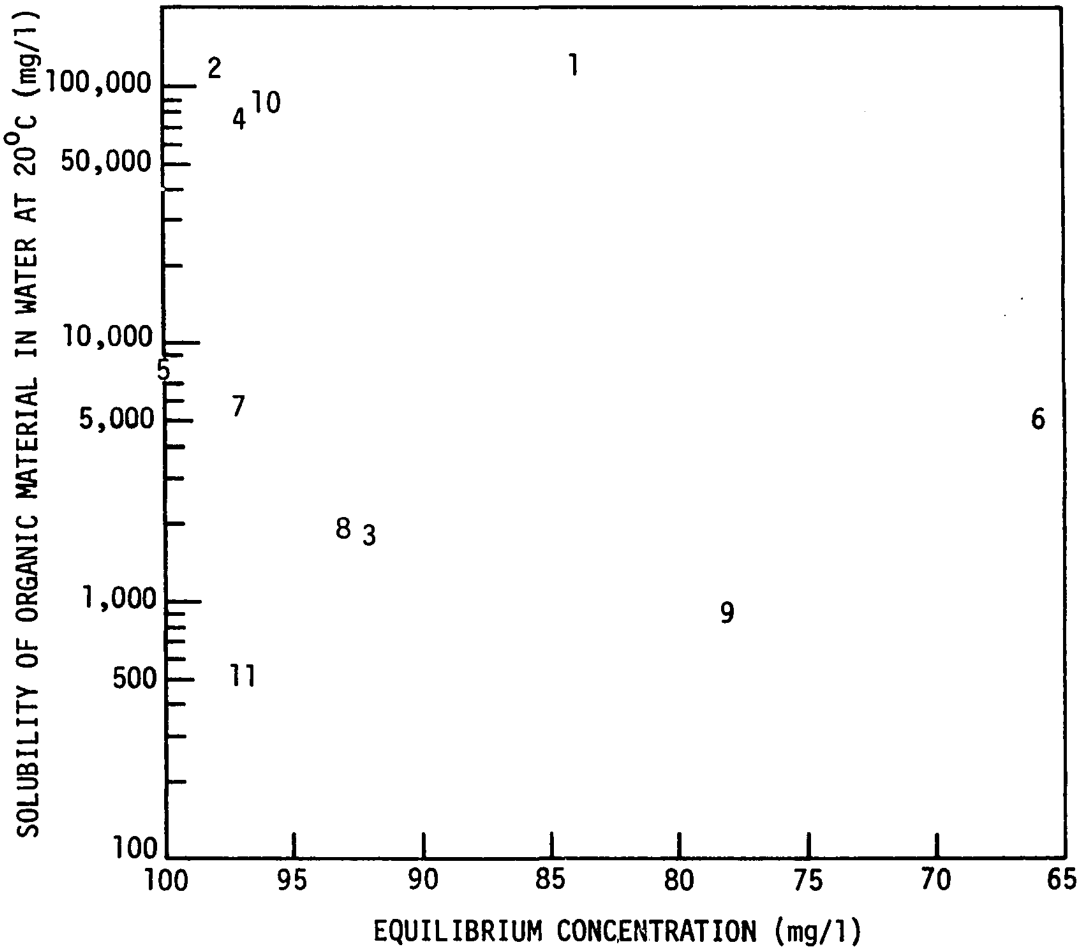

Fig. 25a. **Solubility versus equilibrium concentration for the organic pollutants adsorbed on DAM from an initial organic solution concentration of 100 mg/l**

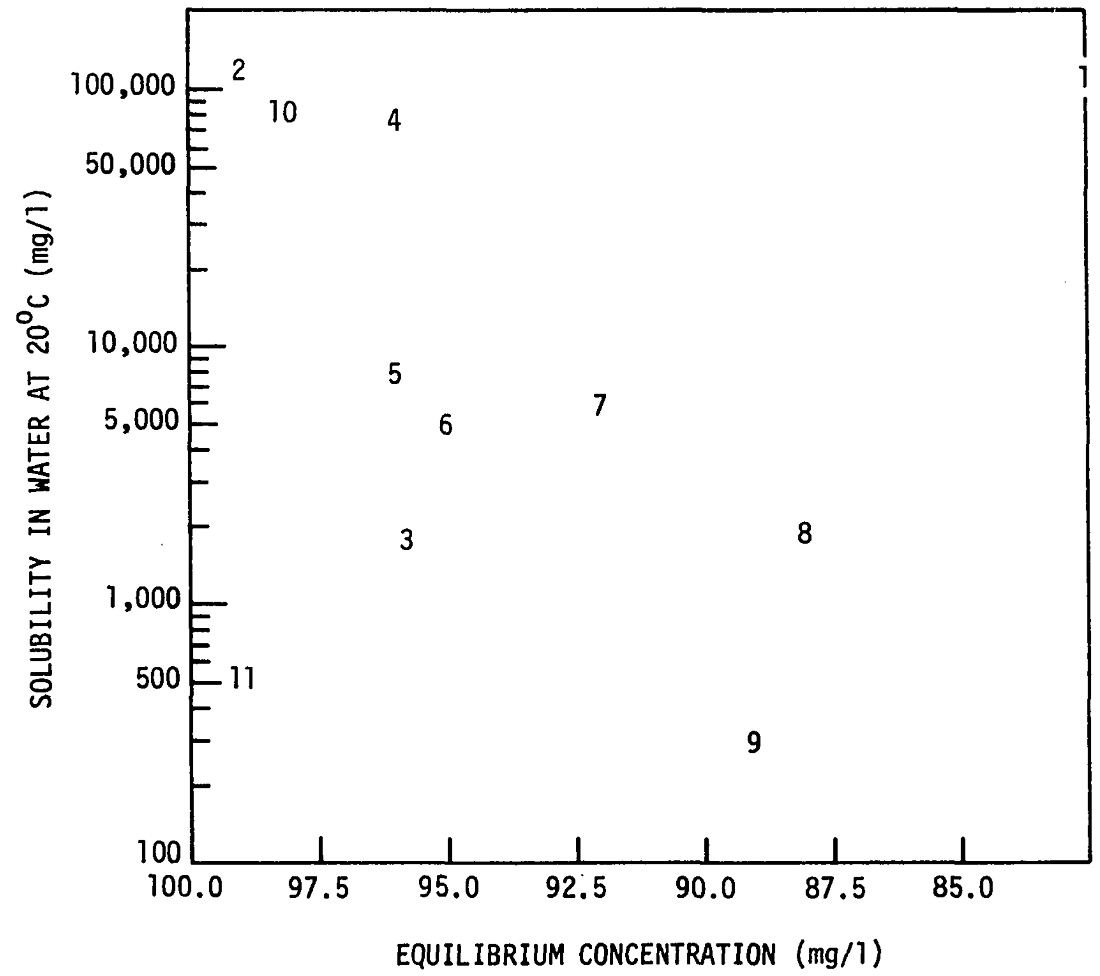

Fig. 25b. Solubility versus equilibrium concentration for the organic pollutants adsorbed on DDAM from an initial organic solution concentration of 100 mg/l

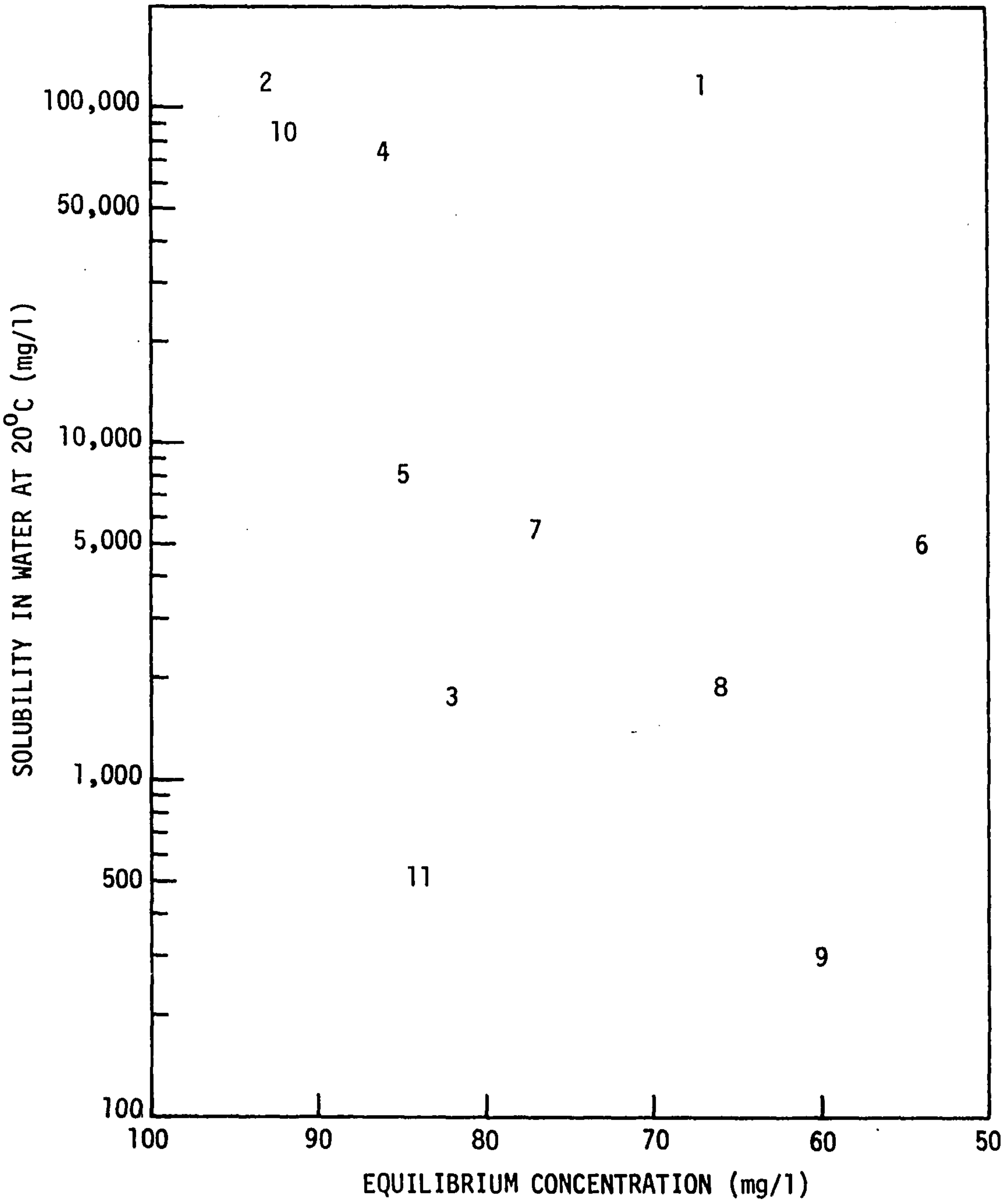

Fig. 25c. Solubility versus equilibrium concentration for the organic pollutants adsorbed on PAM from an initial organic solution concentration of 100 mg/l

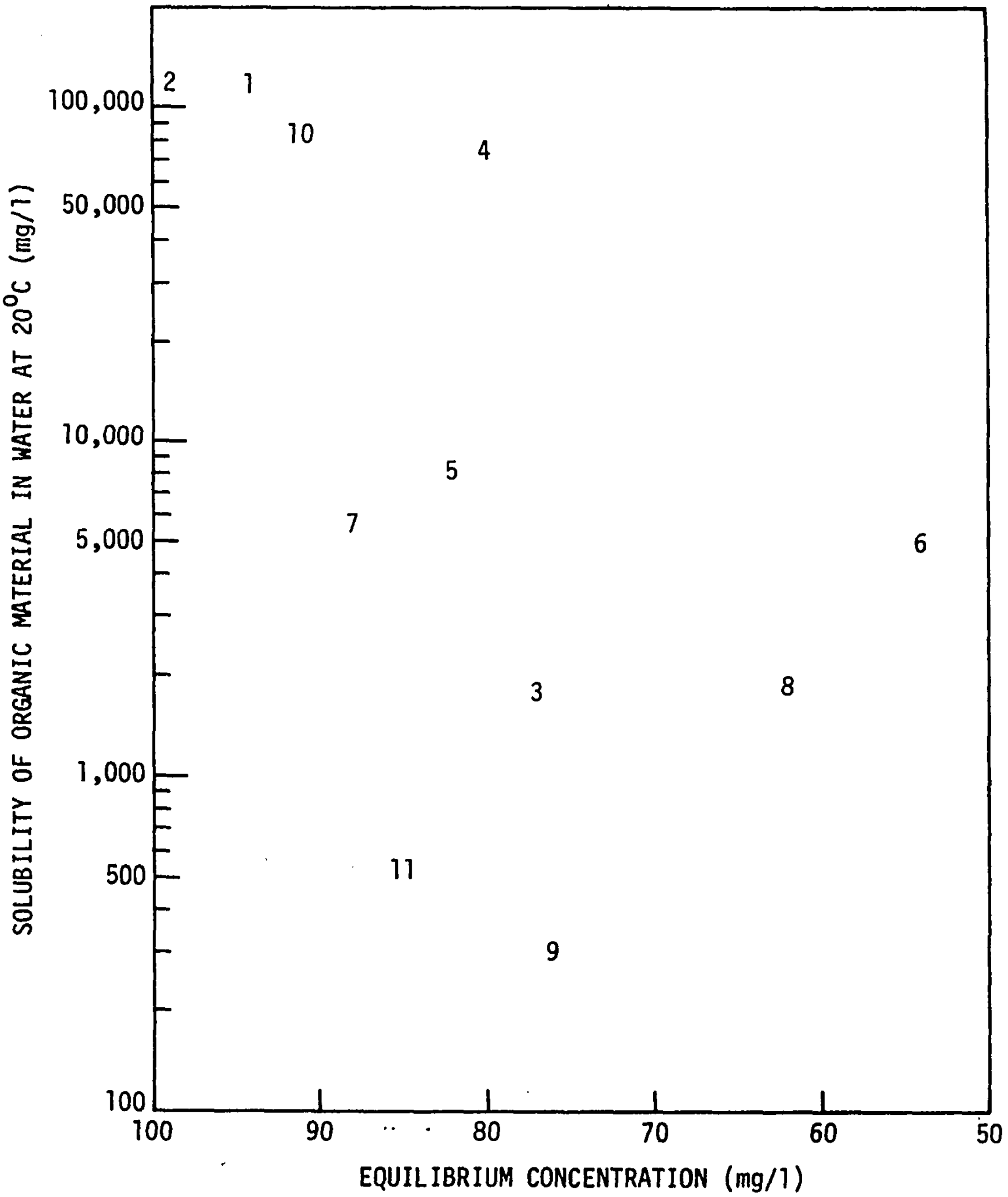

Fig. 25d. Solubility versus equilibrium concentration for the organic pollutants adsorbed on montmorillonite from an initial organic solution concentration of 100 mg/l

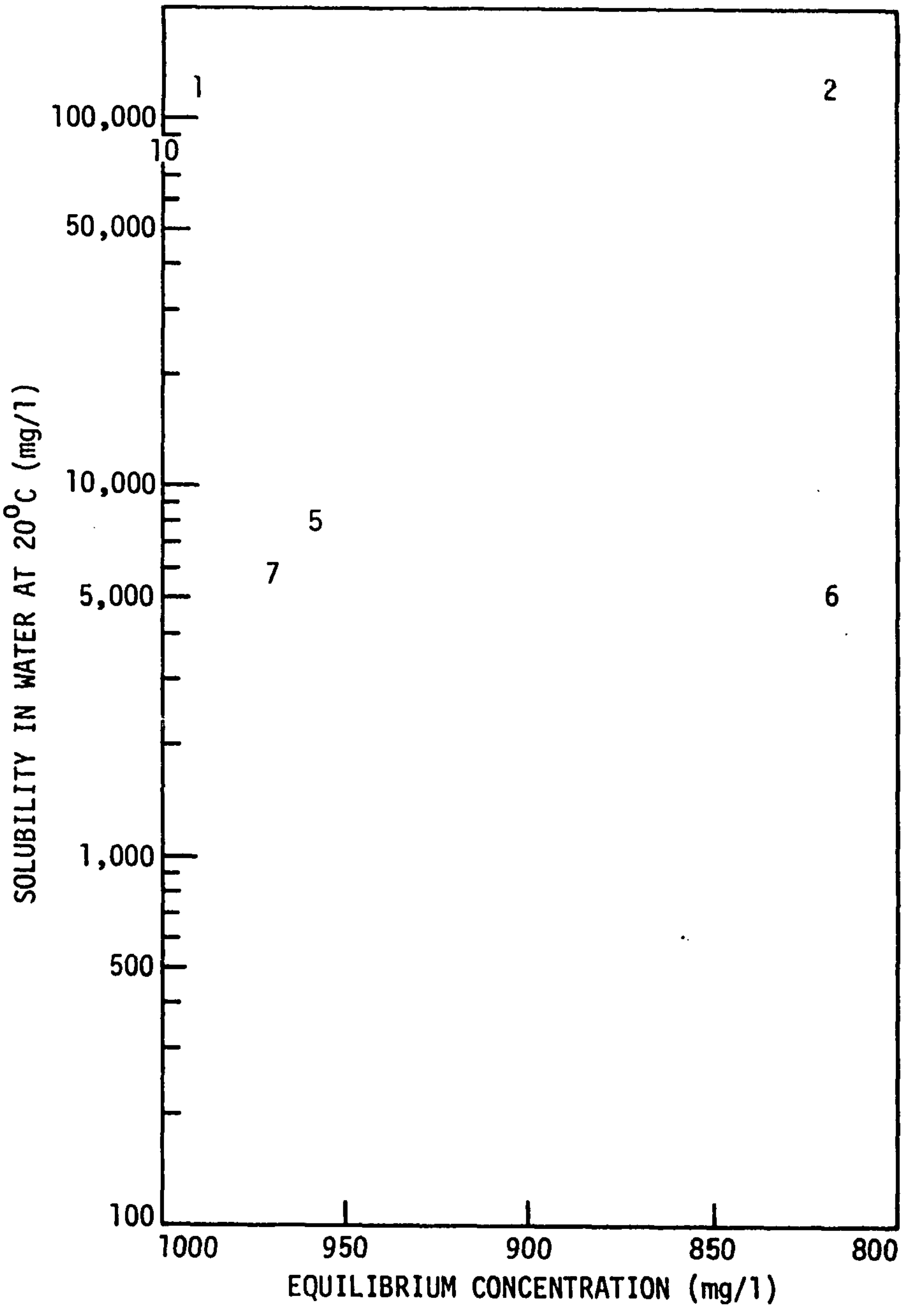

Fig. 26a. Solubility versus equilibrium concentration for the organic pollutants adsorbed on DAM from an initial organic solution concentration of 1,000 mg/l

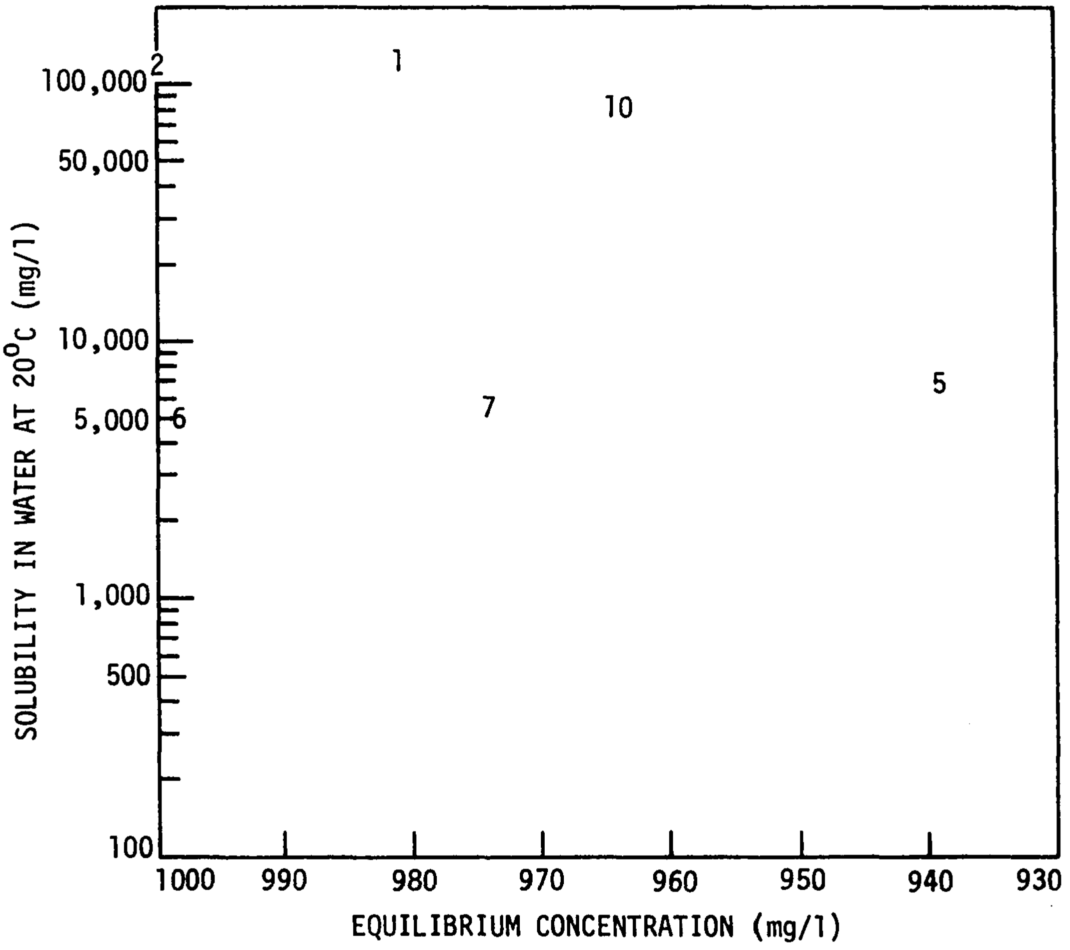

Fig. 26b. Solubility versus equilibrium concentration for the organic pollutants adsorbed on DDAM from an initial organic solution concentration of 1,000 mg/l

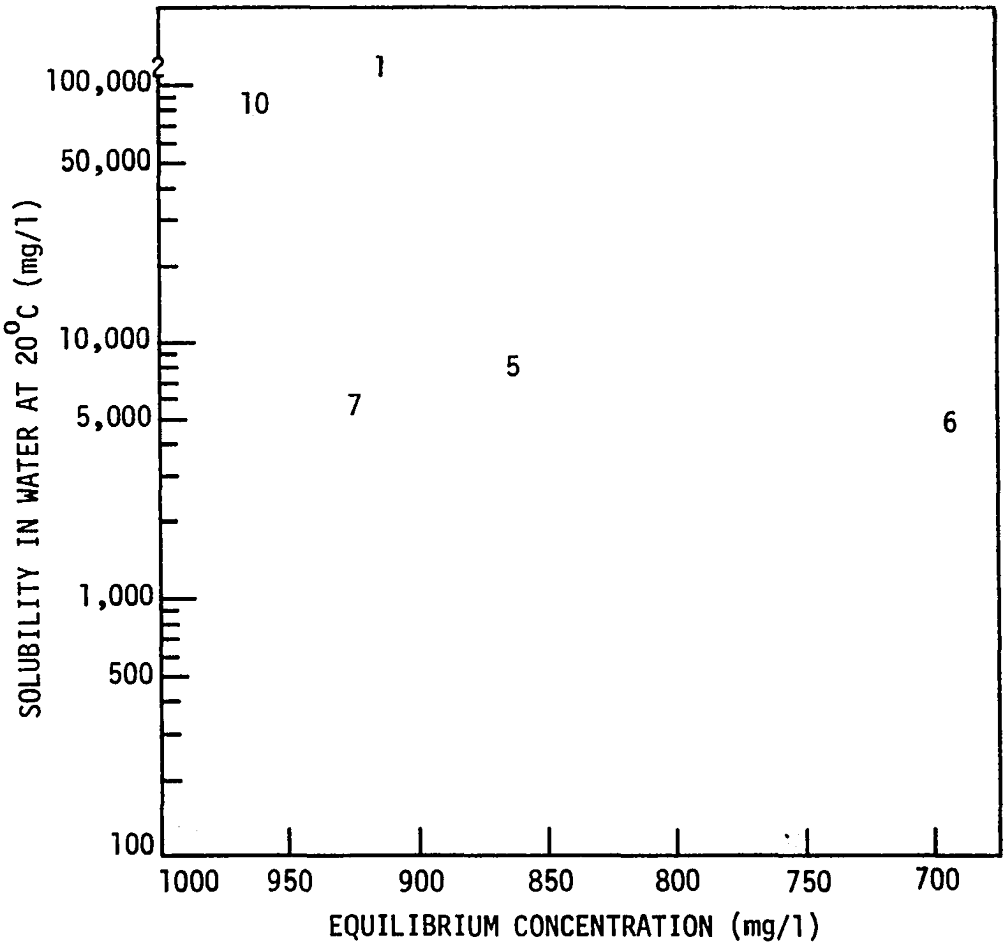

Fig. 26c. Solubility versus equilibrium concentration for the organic pollutants adsorbed on PAM from an initial organic solution concentration of 1,000 mg/l

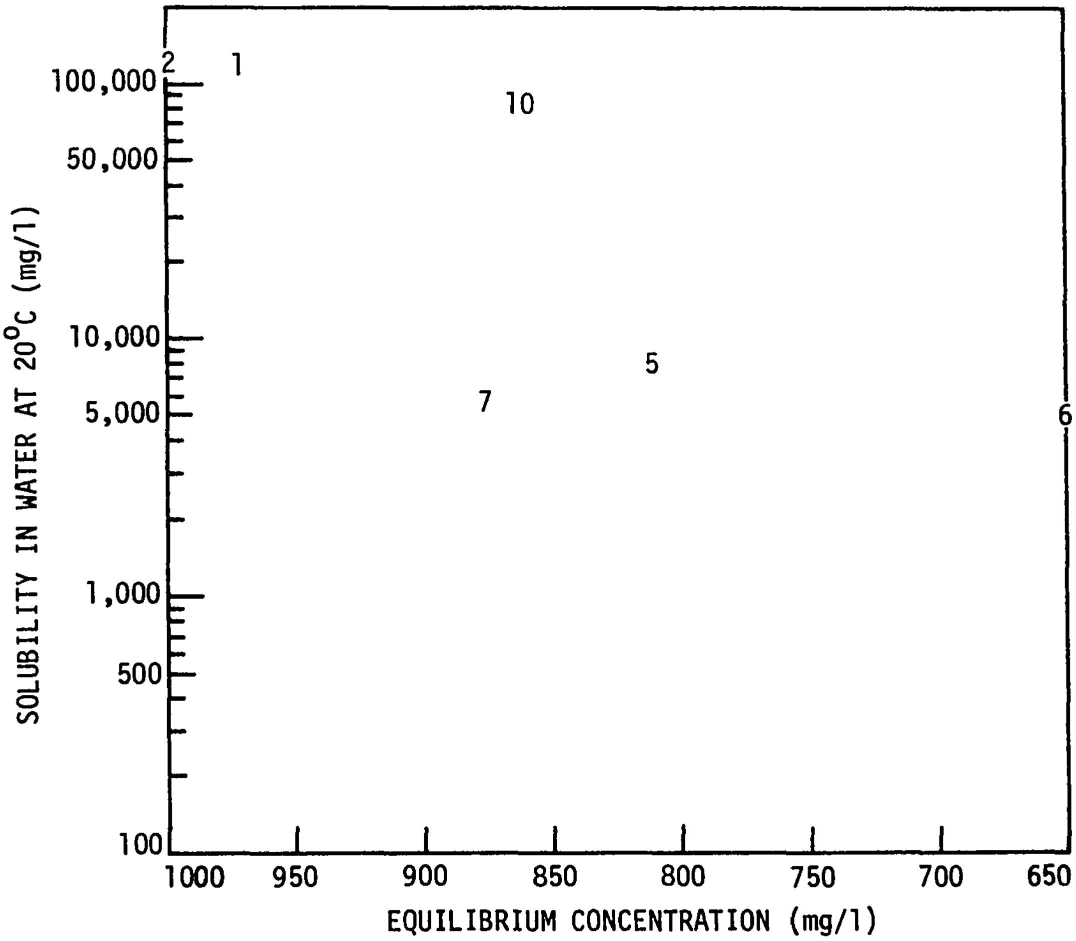

Fig. 26d. Solubility versus equilibrium concentration for the organic pollutants adsorbed on montmorillonite from an initial organic solution concentration of 1,000 mg/l

Acetaldehyde [1] and dimethylphthalate [6] deviate significantly from this pattern, but this development is explainable with additional information beyond that of solubility. In the case of acetaldehyde [1], it does not show marked adsorption on the untreated montmorillonite. The fact that it was adsorbed by the alkylammonium-montmorillonite is in part due to the formation of an oxime, an unstable condensation product that results when acetaldehyde chemically reacts with the alkylammonium ions in the interlamellar spaces of the alkylammonium-clays. This was especially noticeable in a few samples with dodecylammonium-montmorillonite, as the isotherm solution turned a bright yellow color. Confirmation of the fact that alkylammonium ions reacted with intercalated acetaldehyde was noted when the samples were filtered. The filter effluent was clear and the montmorillonite retained on the filter paper was a yellow color. Further indication of the possible formation of an oxime is evident from the basal spacings of dodecylammonium-montmorillonite in the isotherm conducted with an initial organic solution concentration of 1,000 milligrams per liter, Table 10, where the dodecylammonium-montmorillonite did not return to its usual 14.6 to 14.7 basal spacing after drying. Ketones also have the ability to form oximes when contacted with ammonia derivatives, but no such reaction was observed with acetone and the alkylammonium-montmorillonites. The other wide deviation from this pattern, dimethylphthalate [6], was observed with all the clays except dodecyldiammonium-montmorillonite. This appeared to be attributable to the fact that dimethylphthalate penetrated the interlamellar spaces of all the montmorillonites except dodecyldiammonium-montmorillonite. The phenomenon is evident from the basal spacings in Table 9 for the different clays reacted with dimethylphthalate.

The data for the isotherms performed at an initial organic solution concentration of 1,000 milligrams per liter, Table 10 and Figures 26a, b, c and d, followed this same pattern, with only the dodecyldiammonium-montmorillonite exhibiting little preference for this ester. There was no evidence to confirm such a reaction, but the affinity shown for dimethylphthalate by two of the alkylammonium-montmorillonites may in part have been due to chemical behavior between the alkylammonium ions and the ester to form an amide. Dodecyldiammonium would have been unable to form an amide complex because it did not undergo further expansion to permit the dimethylphthalate to come in contact with the dodecydiammonium ions already adsorbed in the interlamellar space.

Figures 25a, b, c and d also show the relationship of alcohol chain length, or solubility, and the ability of the montmorillonites to adsorb these alcohols. The three alkylammonium-montmorillonites exhibited a stronger preference for the alcohols with increasing alcohol chain length. No such preference was evident with the untreated montmorillonite in Figure 25d. This is to be expected since the alkylammonium-montmorillonites possess interlamellar surfaces of both a hydrophilic and organophilic nature, whereas, the untreated montmorillonite is essentially hydrophilic. These findings are in accord with those of Stul, et al. (121) in a study in which several alcohols were adsorbed on dodecylammonium-montmorillonite. Table 11 lists the millimoles of alcohol adsorbed per gram of dodecylammonium-montmorillonite for this study and for the study by Stul, et al. (121). Although the same alcohol concentrations were not employed in the two studies, there is good agreement among the values within common ranges.

Although significant adsorption of phenol did not occur, the data presented in Table 9 agree quite well with results by Cowan and White (34) and Cowan (32) which indicate 0.007 to 0.047 milligrams of phenol adsorbed per gram of dodecylammonium-montmorillonite at equilibrium concentrations of phenol ranging from 300 milligrams per liter to 3,200 milligrams per liter.

Table 12 (38) presents isotherm results obtained by the wastewater research division of the EPA from 1972 to 1980 for six of the eleven organic compounds adsorbed on activated carbon. Activated carbon displays a larger adsorption capacity for these six compounds at similar organic concentrations than do the four montmorillonites employed in this study, as reported in Table 9. The clays do, however, show preference for the organic pollutants studied and should not be cast aside solely on the basis of these findings.

Probably the most disappointing result of the isotherm study was the poor adsorption shown by dodecyldiammonium-montmorillonite for the eleven organic compounds studied. Weiss (134) suggested that diammonium ions with an equal number of carbon atoms in the alkyl chain would form pillars in the interlamellar space with the alkyl chains oriented at an angle of 56° to the surface, or an ideal cis-trans chain, Figure 3. The dodecyldiammium ions, however, proved to be of the perfect length to satisfy charges on the same surface of the interlamellar space,

Table 11. Comparison of adsorption isotherm results for hexanol and octanol adsorbed on dodecylammonium montmorillonite

Alcohol	Alcohol Equilibrium Concentration (mmole/liter)		Alcohol Adsorbed (mmole/g)	
	Stul, et al. (121)	This Study	Stul, et al. (121)	This Study
Hexanol		0.91		0.029
		0.94		0.010
		0.97		0.000
	4		0.089	
		9.23		0.186
		9.45		0.166
		9.79		0.000
	20.2		1.518	
	22		1.724	
	36		3.251	
Octanol	0.10		0.027	
		0.47		0.077
		0.53		0.084
		0.57		0.123
	0.68		0.308	
	1.00		0.719	
	1.20		0.893	
	1.96		2.00	
	2.0		2.07	
	2.7		4.07	

Table 12. Carbon adsorption isotherm results for six of the eleven organic compounds used in this study (38)

Organic Compound	Initial Concentration, mg/l	Adsorption Capacity, mg/g
Benzene	10	40
	1.0	1.0
	0.1	3×10^{-2}
	0.01	7×10^{-4}
Chloroform	1.0	2.6
	0.1	0.48
	0.01	9×10^{-2}
	0.001	2×10^{-2}
Dimethyphthalate	10	250
	1.0	97
	0.1	38
	0.01	15
Nitrobenzene	10	180
	1.0	68
	0.1	25
	0.01	9.3
Phenol	10	74
	1.0	21
	0.1	6.0
	0.01	1.7
Toluene	1.0	26
	0.1	9.4
	0.01	3.4
	0.001	1.2

thus it did not expand the clay significantly but tended to lie flat in the interlamellar space and to prevent the clay from undergoing further expansion when contacted with the organic pollutants.

X-Ray Expansion Study of Eleven Organic Compounds Adsorbed on Alkylammonium-Bentonites and Wyoming Bentonite

Many of the eleven organic compounds interacted with the alkylammonium montmorillonites and montmorillonite in the isotherm study were adsorbed from ten to fifty percent as efficiently as they could be adsorbed on activated carbon. It appeared in at least some of the cases that concentrations employed in the isotherm study were not high enough to permit the larger organic molecules to further expand the clay lattices to generate adsorption on the large interlamellar surface areas of the clays.

Concentrations from 0 to 100 percent of the organics in distilled water were contacted with the Wyoming bentonite and the alkylammonium-bentonites, prepared from Wyoming bentonite without purification, to determine at which concentration further expansion of the various bentonite basal spacings would occur and to determine orientation of the organic molecules in the interlamellar spaces.

Procedures

Significant amounts of alkylammonium-montmorillonites were required to examine the effects of the aqueous solutions of eleven organic compounds on the clay's basal spacings for concentrations of 0.01, 0.1, 1.0, 10.0, 25.0, 50.0, 70.0, and 100 percent. It was not feasible to separate such large amounts of montmorillonite from bentonite by centrifugation, so the alkylammonium salts were adsorbed on Wyoming bentonite in large batch operations. Thirty liters of 0.02 N alkylammonium salt solution were reacted with the appropriate quantity of bentonite under continuous stirring for a forty-eight hour period. The alkylammonium-bentonite was settled for a week and the supernatant was decanted. The bentonite was redispersed in thirty liters of distilled water and continuously mixed for forty-eight hours to remove excess physically adsorbed amine. The suspension was again allowed to settle for a week. The supernatant was decanted and the clay was allowed to air-dry. The dried clay was ground to finer than 200 mesh sieve size with the Shatterbox grinder.

Solutions of the organic pollutants (100 milliliters) were prepared at the desired concentration. The solutions were kept mixed in stoppered 250-milliliter conical flasks with a magnetic stirrer since many of the organic compounds were mixed with the distilled water in concentrations in excess of their solubilities. Enough clay to fill an x-ray sample holder, approximately one gram, was saturated with the organic solution and mixed in a porcelain crucible using a spatula. The saturated clay was spread on an x-ray sample holder with a glass slide, resaturated with the organic solution, and immediately placed in the x-ray diffractometer for analysis.

Results

Table 13 presents the results for the eleven organic compounds adsorbed from organic solution concentrations of 0 to 100 percent on dodecylammonium-bentonite (DAB), dodecyldiammonium-bentonite (DDAB), propylammonium-bentonite (PAB), and Wyoming bentonite. The vivid d_{001} peaks from the x-ray diffraction patterns are listed along with the Miller indices, line breadths, and intensity ratios.

Discussion

Figure 27 presents the approximate size, based on band lengths (133), of the eleven organic compounds and the three alkylamines used in this study. This information, and that provided by Figure 1, can be combined with basal spacings (d_{001} values) and line breadths (B_o values) in Table 13 to determine the orientation of the organic compounds adsorbed in the interlamellar space of the bentonites.

alcohols Results for alcohol "concentrations" below 10 percent indicate the crowding of alcohol molecules between the dodecylammonium ions of DAB causing the dodecylammonium ions to tilt with respect to the silicate surface. This type of orientation is supported by the d_{001} spacings ranging from 17.7 to 18.0 Å.

The alcohol concentration range of 10 to 50 percent is quite interesting as evidence of preferential adsorption[1] is noticed since two distinct d_{001} peaks appear for butanol and hexanol adsorbed on DAB.

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[1] Preferential adsorption refers to a phenomenon that occurs when clays are immersed in a solution consisting of more than one material and some of the clay particles adsorb one of the materials more strongly and other clay particles adsorb another material more strongly, or adsorb the same material to a lesser extent.

Table 13. X-ray expansion study of the eleven organic compounds adsorbed from organic solution concentrations ranging from 0 to 100 percent on the bentonites

	DAB				DDAB				PAB				Bentonite			
Conc. (%)	d_{001}[a] (Å)	hkl[d]	B_o[b] (deg)	I/I_o[c] (%)	d_{001} (Å)	hkl	B_o (deg)	I/I_o (%)	d_{001} (Å)	hkl	B_o (deg)	I/I_o (%)	d_{001} (Å)	hkl	B_o (deg)	I/I_o (%)
Butanol																
1.0	17.7	001	9.8	100	13.1	001	0.5	100	18.0	001	1.2	100	∞	001	-	-
	4.49	004		40	6.55	002		4								
					4.43	003		35								
					3.29	004		23								
10	20.5	001	2.3	100	13.0	001	0.5	100	17.6	001	1.8	100	∞	001	-	-
	3.46	006		56	6.51	002		3	4.44	004		56				
					4.42	003		34	2.97	006		22				
					3.31	004		34								
25	27.6	001	0.6	100	13.3	001	0.55	100	16.7	001	1.7	100	17.7	001	1.4	100
	18.2	001	0.6	75	6.58	002		3	3.29	005		9	4.43	004		227
	14.2	002	0.65	25	4.47	003		34								
	4.48	004		24	3.32	004		22								
50	27.6	001	0.6	100	13.2	001	0.6	100	17.6	001	1.45	100	17.6	001	1.3	100
	17.3	001	0.7	30	6.60	002		3	4.46	004		53	4.41	004		169
	14.0	002	0.65	33	4.44	003		47								
					3.28	004		17								
70	28.5	001	0.8	100	13.4	001	0.65	100	16.8	001	1.2	100	18.0	001	0.95	100
	14.0	002	0.65	35	6.60	002		5					9.1	002		4
					4.46	003		42					4.47	004		28
					3.29	004		23								
100	27.6	001	0.65	100	13.2	001	0.5	100	14.6	001	1.7	100	15.3	001	2.0	100
	18.0	001	0.5	5	6.60	002		3								
	14.0	002	0.6	20	4.44	003		46								
					3.32	004		35								
Hexanol																
1.0	18.0	001	0.75	100	13.5	001	0.55	100	15.7	001	2.5	100	17.0	001	2.0	100
	4.51	004		45	4.48	003		43					4.26	004		8
					3.32	004		28								

10	28.0	001	0.7	100	13.5	001	0.5	100	16.7	001	1.8	100	18.4	001	1.1	100
	14.8	002	1.7	52	6.68	002		3					9.3	002		7
	3.29	008		48	4.47	003		29								
					3.32	004		19								
25	31.0	001	0.6	100	13.4	001	0.5	100	16.1	001	2.1	100	18.8	001	1.0	100
	18.0	001	1.0	22	4.47	003		35								
	15.1	002	0.7	33	3.29	004		20								
50	28.9	001	0.8	100	13.4	001	0.6	100	17.0	001	1.5	100	17.7	001	0.9	100
	14.5	002	1.1	21	3.33	004		32								
70	27.6	001	0.95	100	13.0	001	0.65	100	14.8	001	1.9	100	17.5	001	1.2	100
	13.6	002	0.75	32	6.5	002		6								
100	27.6	001	0.65	100	13.4	001	0.7	100	14.7	001	1.5	100	15.2	001	1.9	100
	13.6	002	0.7	40	4.47	003		81								
					3.33	004		52								
Octanol																
1.0	17.8	001	1.0	100	12.8	001	0.8	100	15.2	001	2.4	100	17.7	001	1.7	100
10	17.8	001	0.85	100	13.4	001	0.55	100	16.7	001	2.0	100	29.9	001	0.5	100
					3.35	004		72					18.8	001	1.0	200
25	32.7	001	0.6	100	13.3	001	0.55	100	31.0	001	0.9	100	19.2	001	1.1	100
	16.3	002	0.6	47	3.32	004		46	17.8	001	0.9	17				
	10.9	003		10					15.2	002	1.1	32				
50	32.0	001	0.8	100	13.4	001	0.6	100	32.0	001	1.1	100	18.8	001	1.1	100
	15.8	002	0.7	40	3.32	004		30	16.7	001	1.8	263				
70	34.0	001	0.9	100	13.2	001	0.65	100	14.7	001	1.6	100	16.2	001	1.6	100
	15.8	002	0.8	25	6.55	002		6								
					4.43	003		50								
					3.31	004		32								
100	30.4	001	0.8	100	13.2	001	0.6	100	14.0	001	1.0	100	14.1	001	1.3	100
	14.7	002	0.7	27	6.51	002		3								
	9.8	003		4	4.41	003		42								
					3.30	004		22								

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[a] Basal spacing in angstroms.

[b] Miller indices.

[c] Line breadth in degrees.

[d] Ratio of the intensity of $d_{00\ell}$ peaks to the intensity of the d_{001} peaks.

Table 13. continued

Conc. (%)	DAB				DDAB				PAB				Bentonite			
	d_{001}[a] (Å)	hkl[d]	B_o[b] (deg)	I/I_o[c] (%)	d_{001} (Å)	hkl	B_o (deg)	I/I_o (%)	d_{001} (Å)	hkl	B_o (deg)	I/I_o (%)	d_{001} (Å)	hkl	B_o (deg)	I/I_o (%)
Benzene																
0.01	16.4	001	1.2	100	13.1	001	0.6	100	18.4	001	1.5	100	∞	001	-	-
					6.55	002		3	13.4	001		111				
					3.29	004		21								
1.0	17.7	001	0.75	100	13.2	001	0.65	100	19.2	001	1.2	100	19.2	001	1.5	100
					3.30	004		42	14.2	001	1.6	233	13.9	001	1.0	50
10	17.8	001	0.8	100	12.7	001	0.6	100	18.2	001	2.0	100	19.2	001	1.1	100
	9.11	002		4	6.39	002		4	14.5	001	1.7	154	14.0	001	1.3	64
					3.18	004		54								
25	21.0	001	1.0	100	13.1	001	0.65	100	18.2	001	2.1	100	19.2	001	1.6	100
	16.1	001	1.3	769	6.53	002		6	15.0	001	1.6	89				
					3.28	004		36								
50	16.3	001	1.25	100	13.0	001	0.65	100	15.5	001	1.1	100	15.2	001	1.2	100
					3.28	004		47	5.05	003		4	5.06	003		8
70	16.1	001	1.2	100	13.2	001	0.65	100	15.2	001	1.0	100	20.1	001	1.6	100
					6.58	002		5								
					3.30	004		32								
100	16.1	001	1.4	100	13.0	001	0.5	100	14.9	001	0.75	100	15.0	001	1.1	100
					6.46	002		6	4.99	003		10	5.03	003		6
					3.26	004		48								
Toluene																
0.01	16.2	001	1.3	100	13.2	001	0.5	100	17.7	001	1.6	100	∞	001	-	-
					6.57	002		2	13.4	001		200				
					3.30	004		14								
1.0	17.8	001	0.7	100	13.2	001	0.65	100	19.0	001	1.6	100	18.0	001	1.5	100
					6.58	002		6	14.7	001	1.7	208				
					3.29	004		40								
10	17.7	001	0.75	100	13.3	001	0.55	100	19.2	001	1.7	100	19.2	001	0.8	100
					6.63	002		4	14.6	001	1.6	182				
					4.38	003		23								

					3.29	004		36								
50	16.8	001	0.8	100	13.1	001	0.7	100	15.8	001	2.1	100	19.2	001	1.8	100
					6.53	002		4								
					3.29	004		40								
70	16.4	001	1.3	100	13.1	001	0.6	100	15.5	001	1.2	100	19.2	001	1.2	100
					6.53	002		3								
					4.39	003		25								
					3.29	004		22								
100	16.4	001	1.4	100	13.4	001	0.55	100	14.5	001	1.2	100	14.7	001	1.9	100
					6.63	002		4								
					3.31	004		20								
<u>Nitrobenzene</u>																
0.01	16.7	001	1.1	100	13.1	001	0.55	100	18.0	001	1.3	100	∞	001	-	-
					6.53	002		3	13.2	001		143				
					3.30	004		15								
1.0	17.8	001	0.7	100	13.3	001	0.55	100	18.8	001	1.1	100	19.2	001	1.7	100
					6.58	002		7	14.7	001	2.1	154	15.6	001	1.5	128
					3.29	004		33								
10	26.8	001	0.7	100	13.4	001	0.6	100	15.8	001	2.2	100	16.0	001	1.5	100
	18.4	001	0.9	385	6.55	002		4								
					4.39	003		27								
					3.30	004		33								
25	29.4	001	1.1	100	13.4	001	0.6	100	15.8	001	1.9	100	16.1	001	1.6	100
	14.0	002	0.8	37	4.44	003		30								
					3.30	004		25								
50	28.5	001	1.0	100	13.4	001	0.6	100	15.9	001	1.5	100	16.2	001	1.5	100
	20.5	001	0.75	63	4.43	003		25	5.12	003		17				
	13.9	002	0.75	38	3.30	004		25	3.12	005		30				
70	27.6	001	1.0	100	13.4	001	0.55	100	15.5	001	1.25	100	16.4	001	1.6	100
	13.7	002	0.8	40	6.58	002		5	5.12	003		15				
					4.47	003		38	3.05	005		15				
					3.30	004		25	3.05	005		15				
100	18.4	001	1.2	100	13.4	001	0.55	100	15.2	001	0.75	100	15.2	001	0.8	100
	13.8	001		42	4.45	003		26	5.06	003		23	5.06	003		27
					3.30	004		27	3.05	005		15	3.05	005		23
<u>Phenol</u>																
0.1	16.7	001	1.2	100	13.4	001	0.6	100	18.8	001	1.25	100	∞	001	-	-
					3.31	004		16	13.4	001		200				

Table 13. continued

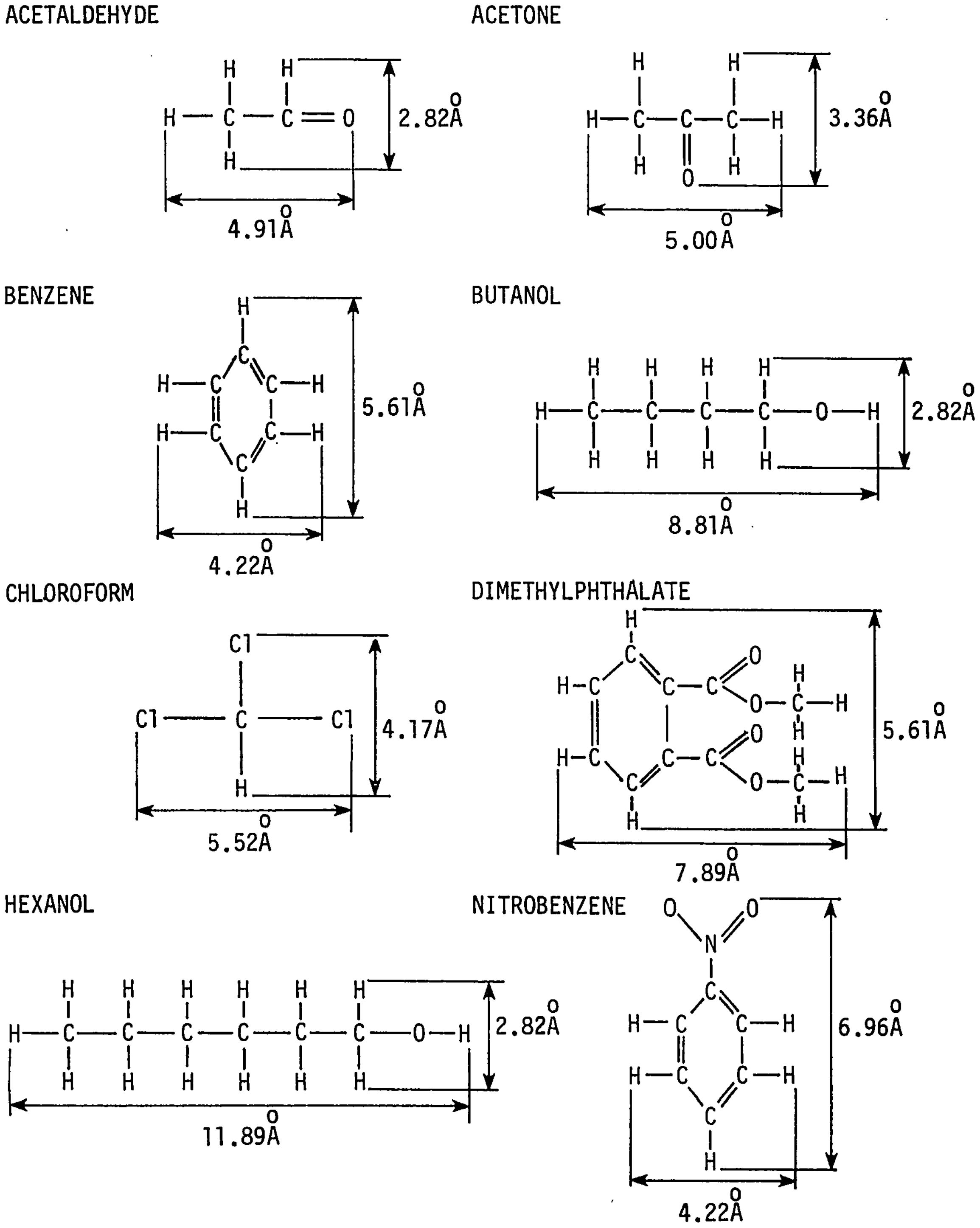
	DAB				DDAB				PAB				Bentonite			
Conc. (%)	d_{001}[a] (Å)	hkl[d]	B_o[b] (deg)	I/I_o[c] (%)	d_{001} (Å)	hkl	B_o (deg)	I/I_o (%)	d_{001} (Å)	hkl	B_o (deg)	I/I_o (%)	d_{001} (Å)	hkl	B_o (deg)	I/I_o (%)
1.0	18.2	001	0.85	100	13.3	001	0.5	100	18.4	001	1.3	100	18.4	001	1.3	100
					6.58	002		5								
					4.39	003		27								
					3.30	004		39								
10	26.4	001	1.3	100	13.1	001	0.5	100	14.9	001	1.1	100	15.2	001	0.7	100
	15.8	001	1.5	133	6.53	002		6								
					4.39	003		46								
					3.29	004		47								
25	31.5	001	0.85	100	13.1	001	0.55	100	15.3	001	1.2	100	15.2	001	1.0	100
	15.5	002	0.8	43	6.57	002		6								
					4.38	003		30								
					3.29	004		44								
50	32.0	001	0.7	100	13.3	001	0.65	100	15.2	001	1.1	100	∞	001	-	-
	15.7	002	0.75	45	6.62	002		5								
	10.6	003		5	4.39	003		36								
					3.29	004		34								
70	32.1	001	0.65	100	13.2	001	0.55	100	15.3	001	1.1	100	27.6	001	1.2	100
	15.5	002	0.7	60	6.51	002		6	5.02	003		18	15.2	001	0.7	50
	10.5	003		8	4.38	003		40								
					3.28	004		36								
100	28.0	001	0.85	100	13.2	001	0.8	100	14.9	001	0.7	100	14.6	001	0.95	100
	14.0	002	0.65	71					7.59	002		40				
									4.97	003		20				
Chloroform																
001	16.9	001	1.1	100	13.4	001	0.6	100	13.4	001	1.2	100	∞	001	-	-
					6.58	002		3								
					3.31	004		16								
0.1	17.0	001	0.8	100	13.1	001	0.5	100	18.0	001	1.3	45	∞	001	-	-
					6.55	002		4	13.4	001		100				
					3.29	004		20	4.47	003		90				
									3.35	004		93				

1.0	17.5	001	0.85	100	13.2	001	0.55	100	19.4	001	1.5	57	20.1	001	1.6	100
					6.53	002		7	14.3	001	1.7	100	15.8	001	0.9	70
					4.41	003		44								
					3.30	004		48								
10	17.6	001	0.7	100	13.2	001	0.55	100	19.0	001	1.5	100	19.6	001	1.0	100
					6.53	002		5								
					3.31	004		35								
25	17.6	001	0.9	100	13.2	001	0.55	100	19.6	001	1.2	66	20.1	001	1.4	100
					6.53	002		5	14.8	001	1.7	100				
					4.41	003		30								
					3.30	004		30								
50	16.9	001	1.1	100	12.9	001	0.55	100	15.4	001	2.1	100	19.6	001	1.5	100
					6.46	002		5					15.5	001	1.0	75
					4.36	003		37								
					3.29	004		37								
70	17.0	001	1.2	100	13.3	001	0.6	100	14.2	001	1.6	100	20.1	001	1.5	100
					6.60	002		4								
					3.31	004		27								
100	16.8	001	1.1	100	13.1	001	0.55	100	13.8	001	1.5	100	13.8	001	2.0	100
					6.53	002		5								
					3.28	004		300								
Dimethylphthalate																
0.01	17.0	001	1.1	100	13.2	001	0.6	100	18.6	001	1.2	34	∞	001	-	-
					6.53	002		3	13.4	001		100				
									6.51	002		8				
0.1	17.8	001	0.6	100	13.3	001	0.55	100	17.5	001	0.55	100	17.8	001	0.65	100
	8.88	002		5	6.55	002		3	8.84	002		11	8.92	002		10
	5.92	003		4	3.30	004		20	5.86	003		7	5.96	003		5
1.0	17.7	001	0.7	100	13.2	001	0.55	100	18.0	001	1.1	100	17.0	001	2.3	100
	9.02	002		3	6.55	002		6	14.2	001	1.2	100				
	6.00	003		3	3.30	004		57								
10	30.4	001	0.55	100	13.4	001	0.7	100	17.3	001	0.7	100	18.4	001	0.6	100
	16.2	002	1.25	37	3.30	004		33	8.88	002	1.0	15	9.16	002	0.6	15
	8.65	003	1.0	11					5.94	003		13	6.06	003	0.5	8
	6.10	005		6					3.56	005		8				
25	28.5	001	0.55	100	13.5	001	0.85	100	17.7	001	0.55	100	18.4	001	0.5	100
	15.2	002	0.6	45					8.88	002	0.5	11	9.20	002	0.5	15

Table 13. continued

	DAB				DDAB				PAB				Bentonite			
Conc. (%)	d_{001}[a] (Å)	hkl[d]	B_o[b] (deg)	I/I_o[c] (%)	d_{001} (Å)	hkl	B_o (deg)	I/I_o (%)	d_{001} (Å)	hkl	B_o (deg)	I/I_o (%)	d_{001} (Å)	hkl	B_o (deg)	I/I_o (%)
	9.93	003	0.65	10					5.92	003	0.6	18	6.10	003	0.6	19
	6.04	005		7					3.56	005		7	3.64	005		6
50	29.9	001	0.55	100	13.6	001	1.0	100	17.5	001	0.65	100	17.8	001	0.5	100
	15.5	002	0.6	46					8.84	002	0.75	20	9.06	002	0.6	20
	10.0	003	0.6	10					5.90	003		25	6.06	003	1.7	30
	6.04	005		6					3.56	005		15	3.63	005		15
70	28.5	001	0.55	100	13.3	001	0.9	100	17.3	001	0.7	100	18.2	001	0.5	100
	15.1	002	0.6	35					8.80	002	0.8	11	9.11	002	0.45	17
	10.0	003	0.6	8					5.86	003		11	6.06	003	0.4	13
	6.04	005		15					3.54	005		8	3.64	005		7
100	28.5	001	0.6	100	13.6	001	0.85	100	17.7	001	0.6	100	18.4	001	0.45	100
	14.9	002	0.6	45					8.88	002	0.5	18	9.11	002	0.4	20
	9.99	003	0.8	13					5.92	003		16	6.08	003	0.5	15
	6.02	005		10					3.57	005		10	3.64	005		7
Acetaldehyde																
0.01	16.4	001	1.2	100	13.3	001	0.55	100	17.8	001	1.0	25	∞	001	-	-
					6.58	002		2	13.4	001		100				
					3.32	004		13	6.49	002		2				
0.1	16.1	001	1.5	100	13.4	001	0.55	100	17.8	001	0.9	24	∞	001	-	-
					6.68	002		2	13.6	001		100				
					3.31	004		15								
1.0	17.6	001	0.7	100	13.2	001	0.55	100	18.6	001	1.3	70	∞	001	-	-
					6.53	002		5	14.2	001	1.9	100				
					3.30	004		29								
10	17.5	001	0.9	100	13.2	001	0.6	100	20.1	001	1.4	63	∞	001	-	-
					6.53	002		5	14.2	001	1.5	100				
					3.28	004		75								
25	18.0	001	0.9	100	13.3	001	0.8	100	14.0	001	2.0	100	∞	001	-	-
					3.30	004		40								
50	18.6	001	1.1	100	13.1	001	0.55	100	15.0	001	1.5	100	∞	001	-	-
					6.53	002		3								
					3.29	004		32								

70	29.9	001	0.65	100	13.0	001	0.65	100	30.4	001	0.95	65	31.0	001	1.6	100
	17.0	001	1.3	100	6.48	002		5	16.1	001	1.4	100	16.1	001	1.3	23
	9.8	003		10	3.28	004		30								
100	32.7	001	0.6	100	13.0	001	0.6	100	28.5	001	1.0	100	26.0	001	1.3	100
	17.0	001		84	6.51	002		6	20.1	001	0.75	75	17.3	001		25
	10.8	003		9	3.28	004		28								
Acetone																
0.01	16.7	001	1.1	100	13.0	001	0.5	100	18.2	001	1.0	20	∞	001	-	-
					6.52	002		3	13.1	001		100				
					3.29	004		20	6.41	002		5				
0.1	16.5	001	1.2	100	13.3	001	0.6	100	18.4	001	0.85	15	∞	001	-	-
					6.55	002		3	13.0	001		100				
					3.30	004		15	6.41	002		5				
									3.24	004		30				
1.0	17.3	001	0.65	100	13.2	001	0.6	100	18.8	001	1.3	100	∞	001	-	-
					6.63	002		5	14.7	001	1.5	85				
					3.30	004		30								
10	17.8	001	0.7	100	13.4	001	0.7	100	17.8	001	1.3	80	∞	001	-	-
					6.55	002		3	14.2	001	1.5	100				
					3.30	004		40								
25	18.4	001	0.8	100	13.2	001	0.65	100	14.3	001	1.8	100	∞	001	-	-
					6.55	002		5								
					3.30	004		40								
50	24.2	001	1.1	100	13.3	001	0.55	100	13.9	001	1.1	100	13.7	001	1.0	100
	18.2	001	1.1	55	6.55	002		4								
	13.6	002		20	3.30	004		25								
	9.06	002		15												
70	27.6	001	0.55	100	13.2	001	0.65	100	14.0	001	1.4	100	27.6	001	1.5	100
	17.8	001	0.65	22	6.53	002		7					16.4	001	0.5	18
	13.9	002	0.7	18	3.30	004		30								
	9.25	002		7												
100	30.4	001	0.7	50	13.3	001	0.6	100	14.0	001	1.3	100	21.8	001	0.9	100
	18.0	001	0.75	100	6.53	002		5					18.0	001	1.0	75
	14.0	002	0.65	50	3.28	004		45					14.0	001	0.9	25



ACETALDEHYDE

ACETONE

BENZENE

BUTANOL

CHLOROFORM

DIMETHYLPHTHALATE

HEXANOL

NITROBENZENE

Figure 27. Approximate size, based on bond lengths (133), of the eleven organic compounds and the three amines used in this study

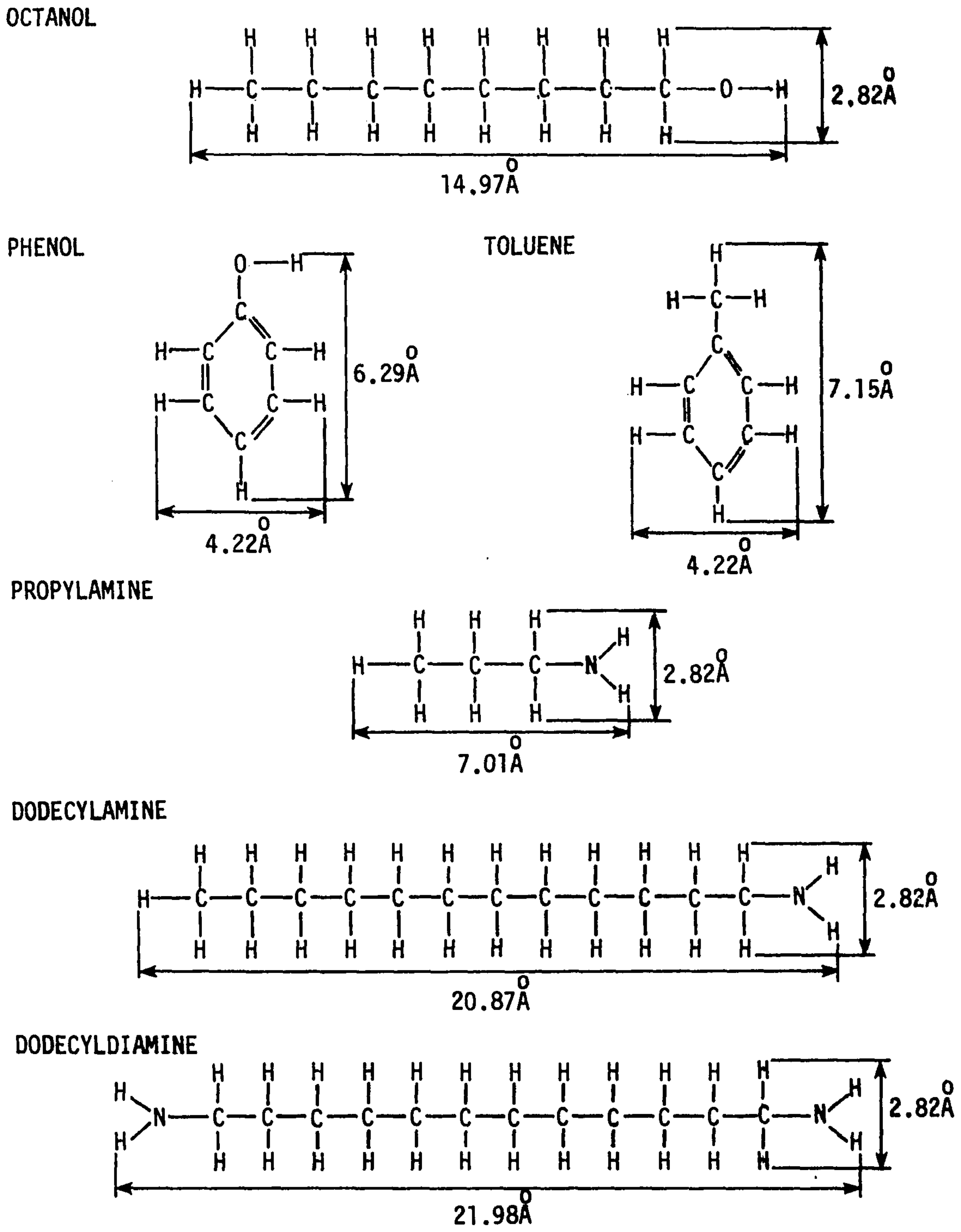


Figure 27. (continued)

This change in the pattern of d_{001} peaks for increasing concentrations of butanol adsorbed on DAB is apparent in Figure 28a. Figures 28b, c, and d for the adsorption of butanol on DDAB, PAB, and Wyoming bentonite do not exhibit this pattern of two separate, distinct d_{001} peaks.

The two ranges of d_{001} spacings from 17.3 to 18.2 Å, and from 27.6 to 31.0 Å suggest certain clay particles are forming a one-layer complex and other clay particles are forming two-layer complexes with butanol and hexanol in the interlamellar space of DAB. The basal spacings indicate that in both complexes the zig-zag of the alcohol chains is fitted between dodecylammonium ions and is oriented perpendicularly to the silicate surface. Such an orientation implies hydrogen bonding of the alcohol hydroxyl groups to oxygen atoms on the silicate surfaces.

Octanol adsorbed on DAB did not exhibit preferential adsorption and formed either one or two-layer complexes in the interlamellar space depending on the octanol solution concentration. Uniform, two-layer interlamellar complexes were also formed by hexanol adsorbed on the DAB when the alcohol concentrations were 50 percent and higher.

The basal spacings obtained for adsorption of the alcohols on DAB match the basal spacings calculated from values in Figures 1 and 27, assuming a shortening of the alcohol chains by kinking as others have noted for the adsorption of alcohols on montmorillonite (43, 51, 52, 80). These results are also in accordance with findings by Stul, et al. (121) in which several alcohols were adsorbed on dodecylammonium-montmorillonite. The interpretation of the results are slightly

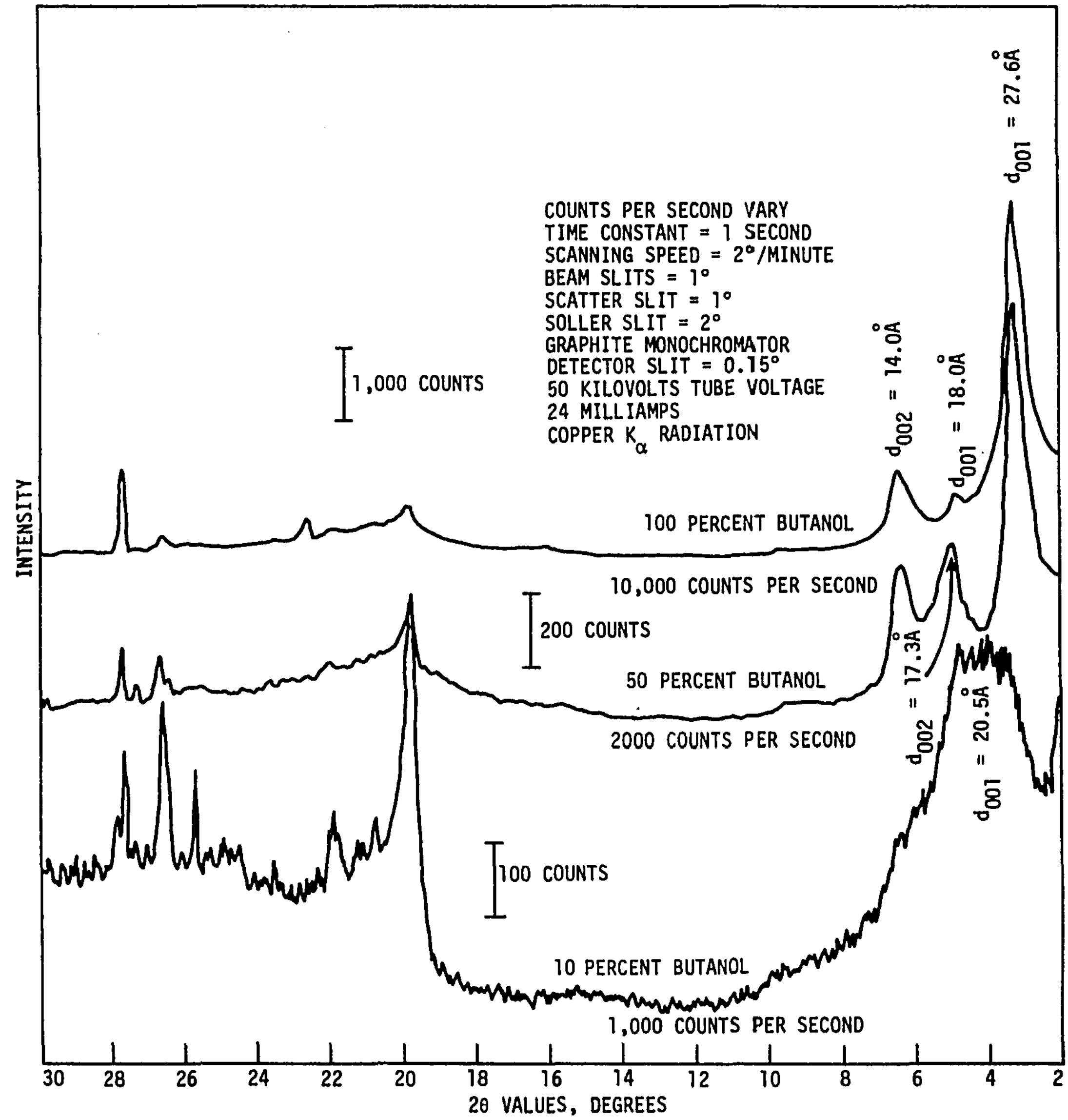


Fig. 28a. Selected diffraction patterns for the x-ray expansion study of butanol adsorbed on DAB

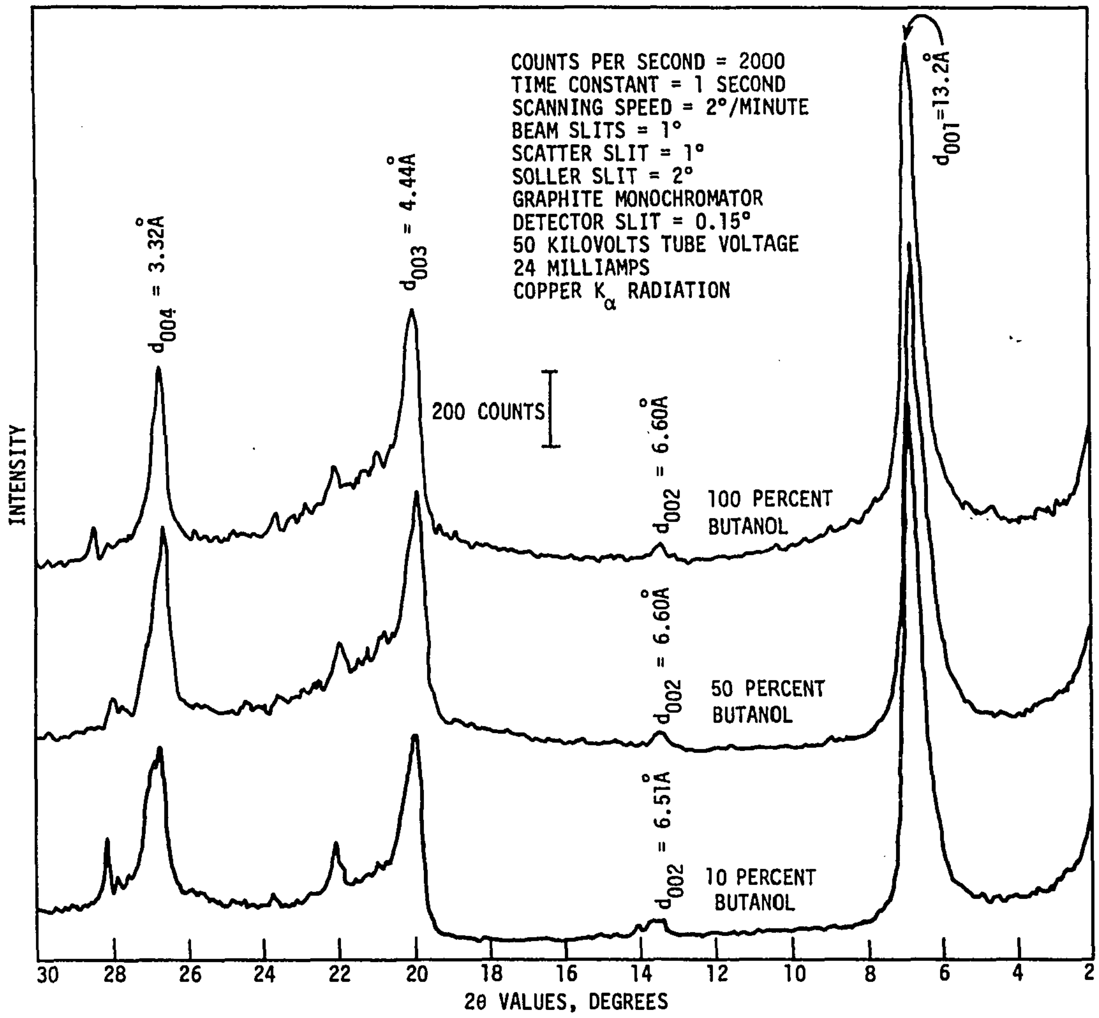


Fig. 28b. Selected diffraction patterns for the x-ray expansion study of butanol adsorbed on DDAB

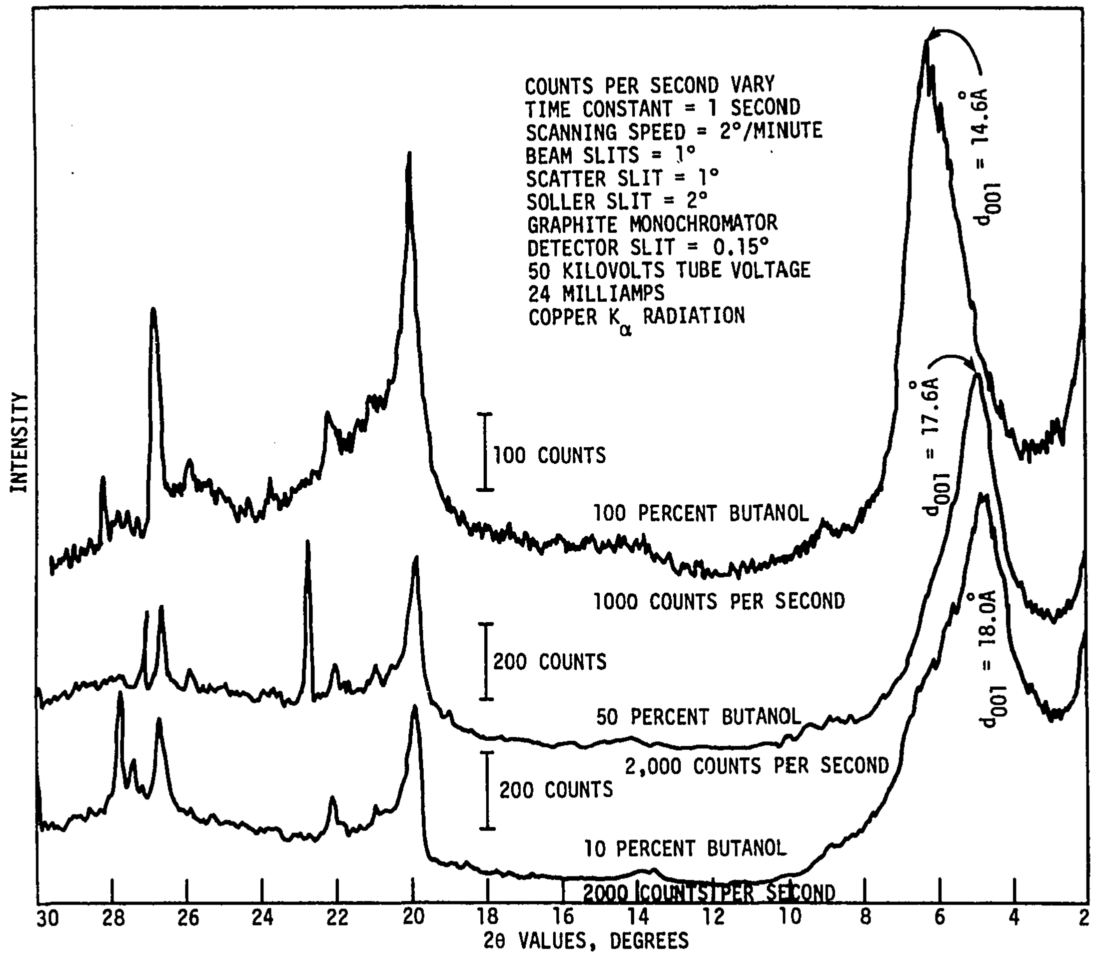


Fig. 28c. Selected diffraction patterns for the x-ray expansion study of butanol adsorbed on PAB

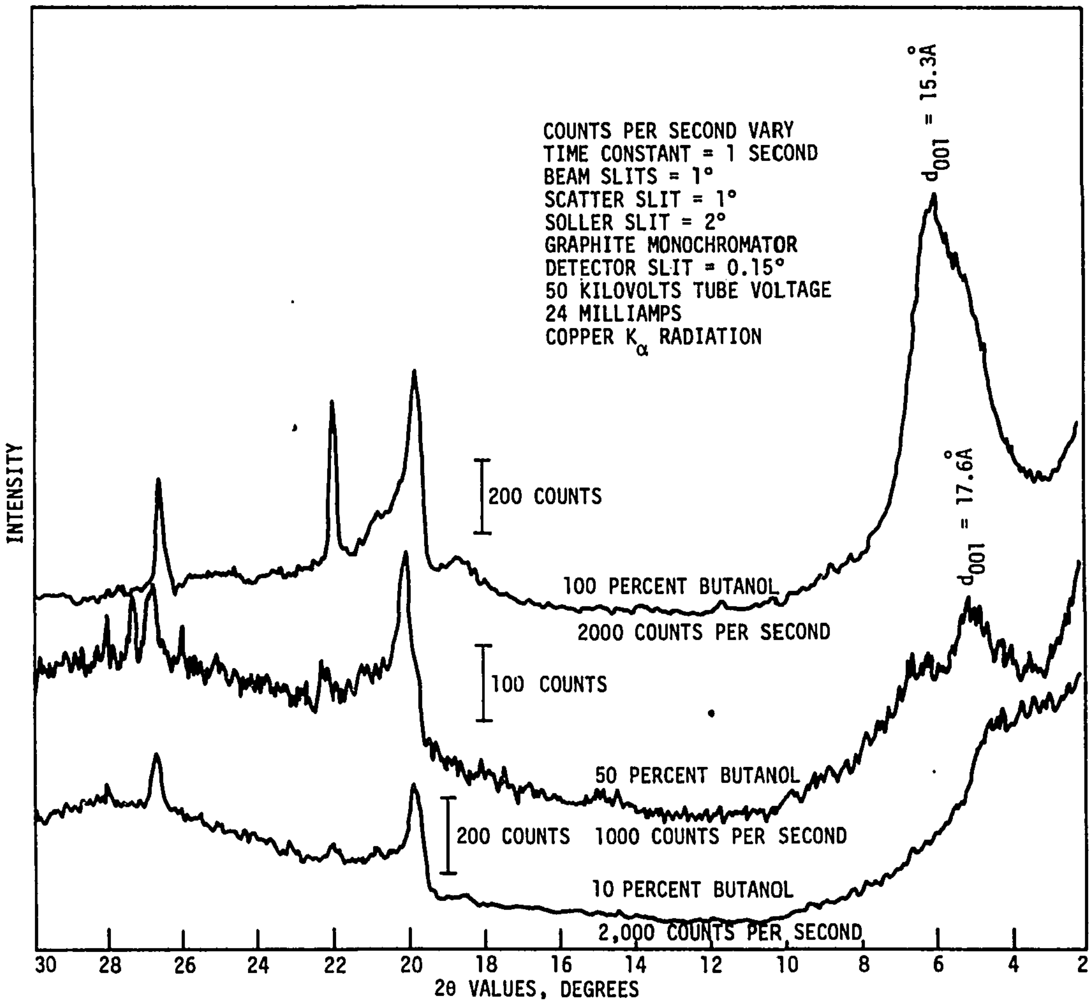


Fig. 28d. Selected diffraction patterns for the x-ray expansion study of butanol adsorbed on Wyoming bentonite

different as Stul, et al. postulated that random interstratification occurred, giving rise to d_{001} spacings calculated from the high spacing d_{001} values and a combined d_{002} spacing calculated from the low spacing d_{001} values and the high spacing d_{002} values. Results from this study seem to suggest preferential adsorption of the alcohols rather than a random interstratification concept.

Basal spacing values indicate that none of the alcohols were able to enter the interlamellar space of dodecyldiammonium-bentonite (DDAB) as this space is completely occupied by the dodecyldiammonium ions which lie flat and satisfy two charges on the same surface of the interlamellar space. These findings are contrary to those of Weiss (134) in which it was suggested the dodecyldiammonium ions formed pillars in the interlamellar space that were oriented at an angle of 56^{o} to the silicate surface.

Propylammonium-bentonite (PAB) and Wyoming bentonite behaved similarly when saturated with the three alcohol solutions. This is not surprising as the propylammonium ion is too small to exhibit much influence on the adsorption of the alcohols in the interlamellar space. Mostly one-layer complexes of the alcohols were formed in the interlamellar space. Octanol did exhibit a combination of one and two-layer complexes at alcohol concentrations in the 10 to 50 percent range. This result is most likely due to the lower solubility of octanol in water and, therefore, its greater preference for adsorption on the clay surface as opposed to butanol and hexanol.

Water influences the ability of the PAB and Wyoming bentonite to incorporate the alcohols in the interlamellar space in two ways. First, d_{001} values decrease to approximately 14.0 to 14.8 Å as the amount of water available in solution decreases, suggesting that water assists in expanding the clay layers, permitting the entrance of the alcohol molecules. Secondly, at butanol concentrations in solution of 10 percent and lower, the water completely expands the clay layers of the Wyoming bentonite and governs the basal spacing. Hexanol and octanol are adsorbed on the Wyoming bentonite even at these low concentrations due to the low solubility of these two alcohols in water.

Aromatic compounds Four of the eleven organics selected for this study; (benzene, nitrobenzene, phenol, and toluene), are aromatic compounds. The intercalation of such molecules is thought to be a process in which all or part of the interlayer water is replaced by the organic species which interact with the interlamellar silicate surfaces through their pi electrons. In dehydrated systems in which the layers of the clay are completely collapsed, intercalation of these organic molecules has been found to proceed with great difficulty (9). For partially dehydrated montmorillonite, Bradley (20), MacEwan (80), and Barshad (15) have shown intercalation of benzene in a double-layer complex, with the plane of the benzene ring lying flat in the interlamellar space. Greene-Kelly (54), on the other hand, found no indication of interlamellar adsorption of benzene on completely dehydrated montmorillonite, but obtained single-layer interlamellar complexes for nitrobenzene and phenol with the plane of the benzene rings oriented perpendicularly to the silicate surface and the nitro and hydroxyl groups projected parallel to the silicate surface.

The results obtained for the expansion study with the different bentonites are essentially the same for benzene and toluene adsorption, and the same for nitrobenzene and phenol adsorption. Such a phenomenon is to be expected since benzene and toluene are nonpolar aromatics, and nitrobenzene and phenol are slightly polar molecules. Doner and Mortland (39) also found benzene and other methyl-substituted aromatics similar to toluene to behave in a like manner when the pure compounds were interacted with montmorillonite.

Basal spacings obtained for the adsorption of benzene and toluene on DAB are slightly larger than the single-layer value of 15.2 Å reported by Barshad (15) for 100 percent benzene adsorbed on montmorillonite, but the water present in this study and the need for the dodecylammonium ions to occupy some of the interlamellar space would account for such increases. The basal spacings in the 16.2 to 18.2 Å range for all four aromatic molecules adsorbed on DAB also may be governed by sufficient crowding of these aromatic molecules into the interlamellar space, causing the dodecylammonium ions to tilt at an angle to the silicate surface, as is the case for water saturated DAB.

Nitrobenzene and phenol also appear to form one-layer complexes with DAB at organic solution concentrations below 1.0 percent. The basal spacings for these low concentration complexes are slightly in excess of that required for the benzene ring lying flat in the interlamellar space since the ring has a thickness of 3.4 Å, but tilting of the plane of the benzene ring, as suggested by Mortland and Pinnavaia (92), would account for these slightly larger basal spacing values. These two aromatic molecules seem to crowd into the interlamellar space at higher concentrations, causing the dodecylammonium ions to stand erect and to govern the basal spacings. Dodecylammonium ions standing erect in the interlamellar space would theoretically produce basal spacings of approximately 30.5 Å. Any tilting or kinking of the hydrocarbon chains would cause the basal spacing values to vary significantly.

None of the four aromatic compounds were able to enter the interlamellar space of the DDAB as this space is completely occupied by the dodecyldiammonium ions as noted previously.

The d_{001} spacing reported in Table 13 for adsorption on PAB and the Wyoming bentonite at a 100 percent organic solution concentration agree quite well with those from previous studies in which adsorption of benzene showed d_{001} spacings of 15.2 Å (15) and 15.1 Å (20), nitrobenzene gave d_{001} spacings of 15.2 Å (54) and 15.3 Å (80), and phenol exhibited a d_{001} spacing of 14.8 Å (54). In the organic concentration range from 0.01 to 70 percent, PAB and Wyoming bentonite exhibited d_{001} spacings ranging from 17.7 to 20.5 Å, except for the 70 percent concentration of phenol adsorbed on Wyoming bentonite which showed a basal spacing of 27.6 Å. Since preferential adsorption is evident throughout this concentration range, it is difficult to determine the exact orientation of the aromatic molecules in the interlamellar space.

Theoretically, from values in Figures 1 and 27, a triple-layer of aromatic molecules lying flat in the interlamellar space would result in a d_{001} spacing of approximately 19.8 Å. If a double-layer complex was formed with the plane of the benzene ring oriented perpendicularly to the silicate surface and the nitro, hydroxyl, and methyl groups projected parallel to the clay surface, as suggested by Greene-Kelly (54), the theoretical d_{001} spacing would be approximately 18.0 Å. Variance of the d_{001} spacings obtained in this study from theoretical ones may also be partially influenced by the presence of water in the interlamellar space.

The x-ray diffraction patterns of phenol adsorbed on the bentonites provided an interesting sidelight as phenol is a crystalline solid at room temperature with a melting point of 41 C (133). Solution concentrations with distilled water were prepared by heating the phenol until it melted, but when the phenol was adsorbed on the bentonites at a 100 percent concentration it solidified and contributed several peaks to the diffraction pattern. Figure 29 presents the x-ray diffraction pattern for 100 percent phenol adsorbed on DAB and the interatomic spacings for phenol at room temperature are listed in Table 14.

Chloroform The basal spacings obtained for the adsorption of chloroform on DAB appear to be independent of the organic solution concentration. This result, along with the poor adsorption capacity shown by DAB for chloroform in Tables 9 and 10, leads to the conclusion that the basal spacings are governed solely by dodecylammonium ions

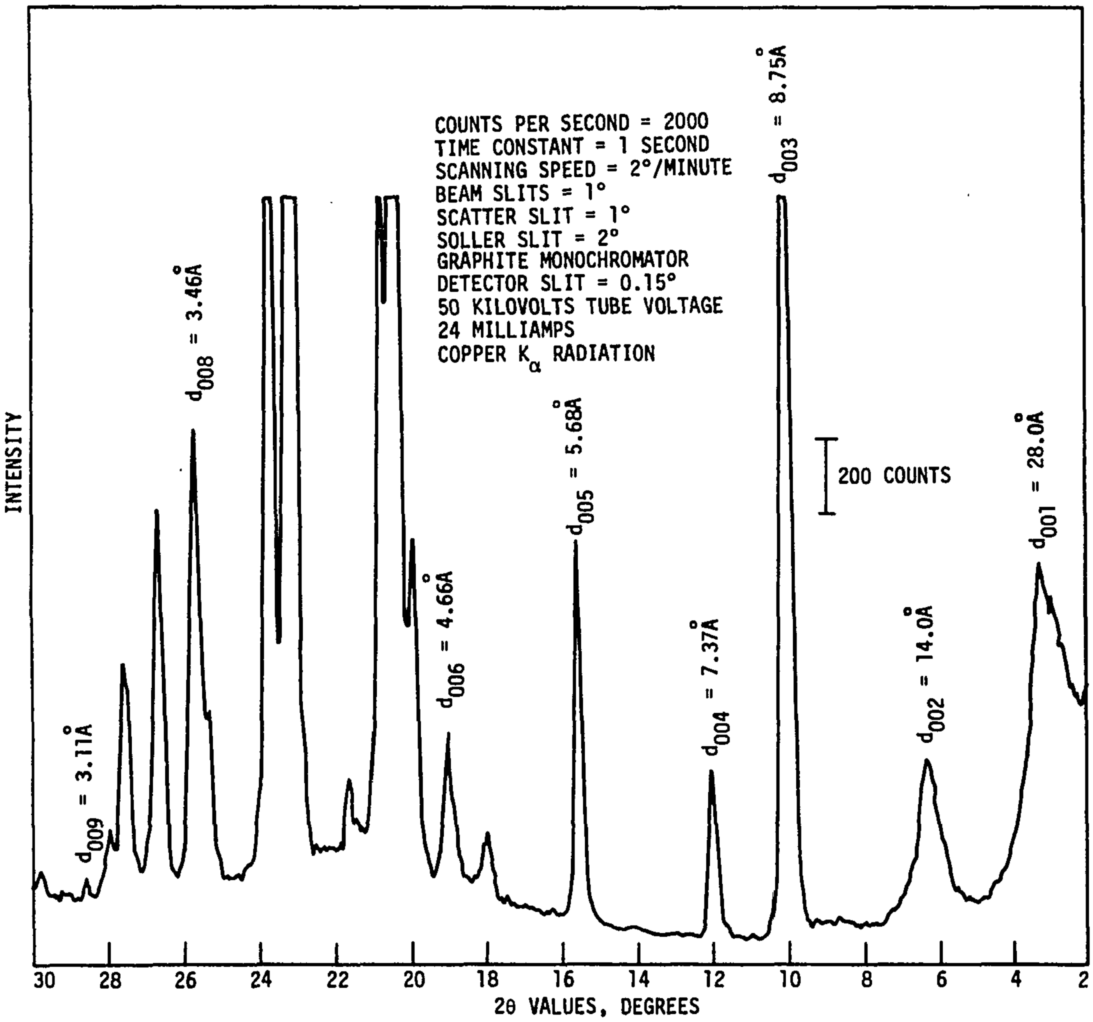


Fig. 29. Diffraction pattern for the x-ray expansion study of 100 percent phenol adsorbed on DAB

Table 14. Interatomic spacings for phenol at room temperature

d, Å[a]	2θ, Degrees	hkl[b]	I/I_o[c]
9.07	9.73	100	100
7.60	11.6	020	20
5.85	15.1	120	14
5.63	15.7	011	2
5.04	17.6	101	25
4.78	18.6	111	45
4.53	19.6	200	25
4.44	20.0	130	95
4.36	20.3	210	30
4.20	21.1	121	12
3.90	22.8	220	100
3.80	23.4	040	85
3.57	24.9	131	16
3.51	25.4	140	20
3.38	26.3	230	14
3.28	27.2	221	18
3.22	27.7	041	8
3.03	29.5	300,002	2
2.959	30.2	310	10
2.912	30.6	240	4

[a] d-spacings in angstroms.

[b] Miller indices.

[c] Ratio of intensity of d_{hkl} peaks to the intensity of the d_{100} peak.

in the interlamellar space which are tilted at an angle to the silicate surface. Water and any chloroform ions entering the interlamellar space fit between the dodecylammonium ions, causing them to assume such a position.

Chloroform was unable to gain access to the interlamellar space of DDAB due to the fact that the interlamellar space was occupied by the dodecyldiammonium ions.

PAB and the Wyoming bentonite reacted similarly when exposed to the chloroform solutions, although water was able to expand completely the Wyoming bentonite at chloroform concentrations below 1.0 percent. Basal spacings in the 18.0 to 20.1 Å range would appear to be a result of a double-layer complex of chloroform in the interlamellar space, with the 4.17 or 5.52 Å dimension, Figure 27, oriented perpendicularly to the silicate surface. The 13.8 to 14.2 Å basal spacing range for adsorption of the 70 and 100 percent chloroform concentrations on PAB and Wyoming bentonite suggest a single-layer of chloroform in the interlamellar space, with the 4.17 or 5.52 Å dimension perpendicular to the silicate surface. The fact that only one layer of chloroform enters the interlamellar space of PAB and Wyoming bentonite at high concentrations is indicative of the role played by water in expanding the silicate layers and helping the chloroform molecules gain access to the interlamellar space.

Dimethylphthalate Results obtained in the isotherm study showed dimethylphthalate to be the most readily adsorbed of all the organics on the dodecylammonium-, propylammonium-, and untreated-montmorillonites. When reacted with DAB at concentrations below 1.0 percent, dimethylphthalate appears to find ample space available between the dodecylammonium ions to form either a double-layer interlamellar complex with the plane of the benzene ring oriented parallel to the silicate surface, or a single-layer complex in which the 7.89 Å dimension of the molecule is oriented perpendicularly to the silicate surface. The former model would appear to be the case, since the diffraction patterns show several $d_{00\ell}$ spacings (d_{001}, d_{002}, d_{003}, and d_{005}) that would result if the dimethlyphthalate molecules were lying flat in the interlamellar space and thus would give use to these diffraction patterns.

The d_{001} spacings ranging from 28.5 to 30.4 Å with dimethlyphthalate concentrations from 10 to 100 percent suggest that the dimethylphthalate molecules have crowded into the interlamellar space in sufficient quantities to cause the dodecylammonium ions to stand erect, with the zig-zag of the hydrocarbon chain oriented perpendicularly to the silicate surface.

DDAB once again showed no signs of further expansion as the dimethylphthalate molecules were unable to gain access to the already occupied interlamellar space.

The d_{001} spacings obtained for dimethylphthalate reacted with PAB and Wyoming bentonite were independent of organic solution concentration. The dimethylphthalate molecules appear to form a double-layer interlamellar complex, with the plane of the benzene ring parallel to the silicate surface. This type of orientation is supported by the large number of $d_{00\ell}$ spacings that appear on the diffraction patterns.

Acetaldehyde and acetone Cation-dipole interactions of an electrostatic nature were suggested by Bissada, et al. (17) as playing an important role in the adsorption of polar organic molecules such as acetaldehyde and acetone on montmorillonite. Bissada, et al. found acetone to form a double-layer complex with montmorillonite, giving a d_{001} spacing of 17.3 Å. MacEwan (80) reported a d_{001} spacing of 17.8 Å for acetone adsorbed on montmorillonite.

Acetaldehyde and acetone adsorbed on DAB show similar behavior. Basal spacings in the range of 16.1 to 16.7 Å, and broad line breadths at organic solution concentrations of 0.01 and 0.1 percent, suggest the formation of an incomplete interlamellar double-layer of these two organic molecules lying with the plane of the molecules flat in the interlamellar space. At organic solution concentrations from 10 to 50 percent, acetaldehyde and acetone molecules become crowded between dodecylammonium ions in the interlamellar space, forcing the dodecylammonium ions to assume a tilted position. Organic solution concentrations above 50 percent cause significant crowding of these two organic molecules in the interlamellar space of DAB, and the dodecylammonium ions are forced into a completely perpendicular position with respect to the silicate surface.

Neither acetaldehyde nor acetone was able to find available space to enter the interlamellar space of DDAB already occupied by the dodecyldiammonium ions.

Acetaldehyde and acetone formed a double-layer complex in the interlamellar space of PAB at organic solution concentrations of 0.01 and 0.1 percent. Preferential adsorption is evident at concentrations of 1.0 and 10 percent, as indicated by the appearance of two distinct d_{001} peaks representative of one and two-layer interlamellar complexes, respectively. Concentrations of 25 and 50 percent show very broad, single peaks that are most likely a combination of d_{001} peaks of both the single and double-layer complexes. The 70 and 100 percent organic concentrations of acetone adsorbed on the PAB continue to follow this pattern. The 70 and 100 percent concentrations of acetaldehyde adsorbed on PAB, however, exhibit large d_{001} spacings, indicative of multilayers of the acetaldehyde adsorbed in the interlamellar space, with as many as four layers of acetaldehyde being taken up in the interlamellar space of the PAB.

Water completely dominates the expansion of the Wyoming bentonite at organic concentrations below 50 percent for adsorption of the acetaldehyde and acetone. Acetone forms a single-layer complex with the Wyoming bentonite at a 50 percent concentration, and both of these polar organic molecules show evidence of multi-layer interlamellar complexes at concentrations of 70 and 100 percent. McAtee, et al. (87) experienced similar multi-layer interlamellar complexes, reporting four layers of benzene, toluene, and acetone adsorbed on methyldioctadecylammonium-montmorillonite, with basal spacings of 31.5, 32.7, and 31.8 Å, respectively.

Additional information of value in determining the mechanism of interaction between the eleven organic pollutants and the four different bentonites is provided by the change in line intensity of the d_{001} peaks at various organic solution concentrations. Since each bentonite sample had to be run on the x-ray diffractometer at the appropriate counts per second range to keep the d_{001} peaks on scale and to minimize instrumental drifts, it is not possible to directly compare the line intensities of the d_{001} peaks. Therefore, the ratios of the line intensity, I, of the bentonite d_{001} peak to the line intensity, I_Q, of the 3.35 Å peak of relatively inert quartz were used for comparison.

The I/I_Q ratio is not completely an ideal means of determining the effect of varying the solution concentration of each of the eleven organic pollutants because it is affected by several factors. Changes in the structure factor and orientation of the clay particles at different organic solution concentrations can influence the I/I_Q ratio. Assuming these effects to be small, the principal factor affecting the I/I_Q ratio is the dilution effect. If the organic material added to the clay sample acts as a dilutant, i.e. the organic does not enter the crystal structure, the I/I_Q ratio should not vary appreciably with increasing organic solution concentration since both clay and quartz are equally diluted. If, on the other hand, the organic material does not act as a dilutant and enters the interlamellar space of the clay, the I/I_Q ratio would increase with increasing organic solution concentrations.

The ability of an organic material to act as a dilutant when mixed with a clay sample can be further explained from another viewpoint. The x-ray beam irradiates an area of a given size on the sample.[1] If the organic material added to the clay sample is not intercalated, the number of crystallites available for diffraction in the irradiated area decreases with increasing organic solution concentrations and the line intensity of the d_{001} peak decreases. When the organic material added to the clay sample is intercalated, the number of crystallites in the irradiated area remains essentially constant with increasing organic solution concentrations. Intercalation of the organic material forms crystallites of a larger size and increases the line intensity of the d_{001} peak, while decreasing the line breadth of this peak.

Table 15 presents the I/I_Q ratios for the eleven organic pollutants adsorbed on DAB, DDAB, PAB, and Wyoming bentonite. Although the ratios are not totally accurate due to the changes occurring in several factors that affect these ratios, general trends can be analyzed to confirm earlier results noted by examining the basal spacing and line breadth values.

The I/I_Q ratios for the alcohols adsorbed on DAB generally increase with increasing organic solution concentrations, confirming that the alcohols are intercalated in first a single-layer interlamellar complex

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[1] The size of the irradiated area is a function of the 2θ angle, but 2θ angles at which the d_{001} peaks appeared in this study did not vary over a wide range.

Table 15. I/I_Q ratios for the eleven organic pollutants adsorbed on DAB, DDAB, PAB, and Wyoming bentonite

Absorbate Concentration (%)	DAB	DDAB	PAB	Bentonite
Butanol				
1.0	8.0	4.3	0.5	-
10	1.2	3.4	3.4	-
25	9.2	4.0	0.-	0.7
50	8.0	2.6	3.8	1.5
70	14	2.5	3.6	6.3
100	27	2.5	2.4	3.0
Hexanol				
1.0	7.5	2.5	3.4	2.5
10	2.1	5.6	2.9	3.5
25	15	4.2	2.0	2.4
50	19	3.8	2.9	5.4
70	10	1.5	2.3	2.3
100	6.8	1.8	1.4	3.6
Octanol				
1.0	17	1.1	1.6	1.7
10	13	1.5	2.1	1.6
25	14	2.2	8.6	2.8
50	8.0	3.1	1.8	1.8
70	23	3.1	2.5	2.0
100	22	3.9	2.7	2.4
Benzene				
1.0	9.2	1.7	6.7	1.6
10	5.4	3.3	1.4	0.7
25	3.3	1.7	1.0	0.5
50	2.7	1.7	2.0	3.8
70	2.7	1.6	2.9	1.3
100	3.3	2.8	2.5	1.9
Toluene				
1.0	8.8	1.6	1.6	1.0
10	13	3.0	3.1	0.6
25	4.5	3.3	1.6	0.3
50	4.4	3.1	0.9	0.2
70	3.1	3.9	6.0	2.7
100	4.2	4.7	2.7	2.6
Nitrobenzene				
1.0	8.3	2.6	2.9	0.9
10	4.4	3.0	1.7	3.1
25	6.0	3.4	2.2	1.8
50	3.6	3.6	3.4	2.0
70	2.7	4.0	4.0	3.3
100	-	4.1	4.4	2.9

Table 15. continued

Absorbate Concentration (%)	DAB	DDAB	PAB	Bentonite
Phenol				
1.0	4.2	3.1	3.3	0.5
10	1.4	2.1	2.8	1.6
25	5.2	3.0	0.2	0.5
50	6.7	3.2	1.8	-
70	5.6	3.6	2.5	0.8
100	1.3	4.0	3.8	1.7
Chloroform				
1.0	5.1	2.5	2.6	0.5
10	8.0	1.7	0.8	0.5
25	4.1	3.4	1.9	0.6
50	2.1	2.9	2.6	1.0
70	2.6	3.0	0.8	0.3
100	3.0	4.0	1.8	1.4
Dimethylphthalate				
1.0	5.0	1.6	2.5	3.3
10	9.4	2.4	5.6	10.1
25	6.3	2.3	5.3	7.8
50	10	1.6	3.5	4.2
70	12	2.0	4.5	7.2
100	6.9	1.4	5.0	10.0
Acetaldehyde				
1.0	5.4	3.4	1.9	-
10	8.8	2.2	2.7	-
25	8.4	2.3	1.5	-
50	4.1	4.0	2.8	-
70	3.3	3.9	6.7	3.0
100	6.0	2.5	1.3	4.4
Acetone				
1.0	4.5	3.5	1.9	-
10	7.2	2.4	2.1	-
25	9.3	2.5	4.3	-
50	4.5	4.1	5.2	2.4
70	6.2	3.7	4.6	1.7
100	20	4.2	12	4.9

and eventually in a double-layer complex. The I/I_Q ratios for the alcohols adsorbed on DDAB show a slight decrease, or remain essentially the same, with increasing organic solution concentrations. This result is due to the lack of intercalation of the alcohols in the interlamellar space of DDAB. The role played by water in helping the alcohols gain access to the interlamellar space of PAB and Wyoming bentonite is noted as I/I_Q ratios tend to increase and then decrease with increasing organic solution concentrations.

I/I_Q ratios for the four aromatic compounds adsorbed on the bentonites tend to decrease or remain essentially the same with increasing organic solution concentrations. Although basal spacing and line breadth values indicated intercalation of the aromatics, except in the case of DDAB, preferential adsorption of these compounds renders the I/I_Q ratios of little value. Therefore, it is difficult to determine any additional information about the mechanism of interaction between the organic pollutants and the clay with any certainty.

The pattern exhibited by the I/I_Q ratios for chloroform adsorbed on DAB suggests that DAB intercalates the maximum quantity of chloroform between the dodecylammonium ions at an organic solution concentration of 10 percent. Larger concentrations of chloroform do not enter the interlamellar space of DAB and act as a dilutant. Preferential adsorption of the chloroform by PAB and Wyoming bentonite render the I/I_Q ratios of little value in providing additional information beyond that already determined from basal spacings and line breadths.

I/I_Q ratios for dimethylphthalate adsorbed on DAB increase up to an organic solution concentration of 10 percent, indicative of the filling of the interlamellar space between dodecylammonium ions by dimethylphthalate. The large I/I_Q ratios at organic solution concentrations of 50 and 70 percent may suggest that these larger concentrations enable the dimethylphthalate to pack between dodecylammonium ions in a more organized pattern. I/I_Q patterns for dimethylphalate adsorbed on DDAB, PAB, and Wyoming bentonite are too erratic to provide any additional information.

The most noticeable result in the I/I_Q ratios for acetaldehyde and acetone adsorbed on the four different bentonites is the large ratios obtained at the 100 percent acetone concentration adsorbed on DAB and PAB. In the case of DAB, the acetone appears to have completely filled interlamellar space available between the dodecylammonium ions, causing these ions to assume an erect position and providing rather large crystallites. The acetone forms a perfect monolayer in the interlamellar space of PAB. Multilayers of acetaldehyde adsorbed in the interlamellar spaces cause a random pattern of the I/I_Q ratios, making it difficult to obtain any additional information about the interaction of this organic with the bentonites.

CONCLUSIONS

It was possible to separate the sodium-montmorillonite fraction from Wyoming bentonite by passing a solution of the bentonite dispersed in distilled water at 25 grams per liter through a Sharples flow through centrifuge at approximately 130 milliliters per minute. The sodium-montmorillonite tended to accumulate on the interior wall of the upper three quarter portions of the centrifuge column, and impurities in the Wyoming bentonite accumulated in the lower portion of the column.

When immersed in hydrochloride salt solutions of dodecyl- and propylamine and dodecyldiamine, the montmorillonite was able to adsorb the alkylammonium ions in the interlamellar space by exchange with the exchangeable sodium cations, causing the clay layers to remain partially expanded when dried. Excess, physically adsorbed alkylammonium ions were removed from the interlamellar space by washing the clay with distilled water, leaving the cation-exchange capacity of the montmorillonite, approximately 94 milliequivalents per 100 grams, satisfied by the alkylammonium ions.

Removal of the excess, physically adsorbed alkylammonium ions also made available additional volume in the interlamellar space to be used for adsorption of organic pollutants in aqueous solution.

Replacement of exchangeable cations on the interlamellar surface of montmorillonite with alkylammonium ions has been shown by several researchers to permit ready intercalation of a wide variety of polar and non-polar organic compounds. Adsorption isotherms conducted at organic solution concentrations of 100 and 1,000 milligrams per liter for eleven organic compounds representing several organic groups showed some indication of intercalation of these organic compounds. Intercalation at these low organic solution concentrations was not sufficient to make the alkylammonium-montmorillonites totally competitive with current adsorbents used in the water and wastewater field, but removal efficiencies from 10 to 50 percent of the efficiency expected for adsorption on activated carbon were obtained.

Organic pollutants found in water and wastewater can definitely be removed from the water to some extent by adsorption on the alkylammonium-montmorillonites. The clays could be added to a sedimentation basin and then settled from solution. Sedimentation of the clays is enhanced to a degree by the treatment with alkylammonium ions, especially the dodecylammonium ion, as these ions cause the clay to become somewhat hydrophobic and make it easier to settle the clays from solution.

X-ray expansion studies performed with the eleven organic compounds adsorbed at high concentrations on the alkylammonium-bentonites and Wyoming bentonite showed significant intercalation as compared to the extent of intercalation observed in the isotherm study. This result suggests that the clays would be more efficient in adsorbing the pollutants from water and wastewater if the pollutants were present at high concentrations. Although an unlikely possibility, it is not completely inconceivable.

Although several studies were cited in this work concerning the adsorption of organic materials on montmorillonite and alkylammonium-montmorillonites, most of these studies have dealt with the pure organic material and not the materials in aqueous solution. Cowan and White (34) and Cowan (32) observed phenol adsorbed from aqueous solution on dodecylammonium-montmorillonite, and Stul, et al. (120, 121) investigated alcohols adsorbed from aqueous solutions on dodecylammonium-montmorillonite. Others have looked at many of the eleven organic compounds studied in this investigation adsorbed from aqueous solution on montmorillonite, but not adsorbed on the alkylammonium-montmorillonites.

Bentonite has been used in the water and wastewater field as a coagulant (98, 99, 100), but few works have been undertaken with the specific objective of utilizing clay to adsorb contaminants from water and wastewater. Williamson, et al. (135) investigated adsorption of the general class of materials contributing to the chemical oxygen demand (COD) of unfiltered and filtered secondary effluent on several clays in the natural state and treated with zinc chloride, phosphoric acid, and a combination of zirconyl chloride and sulfuric acid. Their conclusion was that no cheap, commercially available clay is likely to remove all refractory contaminants found in secondary effluent, at least not as economically as activated carbon does. They noted, however, that clays may be expected to make contributions to advanced wastewater treatment through removal of specific contaminants. El Dib, et al. (42) studied the role of adsorbents in the removal of soluble aromatic hydrocarbons from drinking water using untreated kaolinite and bentonite. Karickhoff, et al. (73) investigated the sorption of hydrophilic pollutants on natural sediments, and McBride, et al. (89) have studied the adsorption of aromatic molecules in aqueous suspension by montmorillonite treated with tetra-alkylammonium ions.

This study has presented an alternative to use of activated carbon and synthetic resins as adsorbents in the water and wastewater field, although admittedly results are preliminary and much experimentation needs to be performed. A quote from McBride, et al. (89) perfectly sums up the conclusions of this study:

> "The results obtained here for the systems studied may or may not be a practical solution for the removal of aromatic species from water; however, the idea of tailoring modified smectites for specific adsorption purposes in improving water quality seems to have promise."

RECOMMENDATIONS FOR FURTHER WORK

Suggestions are boundless for further experimentation with the objective of this research to modify clays to make them practical adsorbents in the field of water and wastewater treatment. Numerous organic cations can be exchanged for exchangeable cations on the interlamellar surface of several clays, each providing its own alteration of the adsorption capacity of the respective clay.

The most promising organic cations are the diammonium ions. Dodecyldiammonium cations used in this study were of the appropriate length to satisfy two charges on the same interlamellar surface and prevented the montmorillonite from undergoing further expansion in the presence of organic pollutants. Diammonium cations of different lengths would not be able to interact with the montmorillonite lattice similarly to dodecyldiammonium cations and may yield a pillar-like structure as suggested by Weiss (134). Such a clay would be in an expanded form, but could posses sufficient free volume in the interlamellar space to intercalate many organic pollutants. In fact, Barrer and Millington (11) have suggested that alkyldiammonium containing less than six carbon atoms would not be of sufficient length to satisfy uniformly spaced charges on the same silicate surface. The eleven organic pollutants studied in this research also represent only a handful of those present in water and wastewater.

This study has concentrated on the exchange of organic cations for the exchangeable cations of the clay lattice. Another area that should be investigated is the exchange of certain inorganic cations on the interlamellar surface of clays. In a recent study, Yamanaka and Brindley (136) exchanged zirconylchloride for sodium ions on montmorillonite and obtained a product with basal spacings near 18 Å which was stable to 500 C and had a surface area in the order of 300 to 400 square meters per gram.

Adsorption studies in this study were performed in aqueous solution. There is some merit to performing the adsorption in vapor phase to determine the thermodynamic characteristics of organic pollutants adsorbed on clays.

The author also investigated briefly the ability of alkylammonium-bentonites and Wyoming bentonite to adsorb organic materials contributing to the biochemical oxygen demand (BOD) of wastewater collected at the Ames wastewater treatment plant before and after it had received primary treatment. Fourteen, liter BOD bottles were filled with 950 milliliters of the wastewater, and 10 milligrams of N-serve were added to each bottle to suppress nitrification. Twelve of the bottles received 100 milligram, 1 gram, and 10 gram portions of the four bentonites. Two bottles served as controls, with one of the bottles containing the wastewater as collected and the other containing supernatant decanted from the collection vessel after permitting the contents to settle for a period of two hours.

The fourteen bottles were placed in an electrolytic BOD apparatus in a constant temperature room at 20 C for ten days. BOD values for the bottles containing the four different bentonites did not show significant differences from the BOD values of the control bottles, but there was some evidence of BOD reduction due to adsorption by the bentonites. A more detailed study in this area of adsorption by clays is warranted.

Another area that may be promising for the use of clays is that of concentrating certain priority pollutants for detection by gas chromatography. Many of the priority pollutants are present in waters at such low concentrations that they must first be concentrated by adsorption on activated carbon and subsequently removed from the carbon in smaller liquid volumes than the volumes from which they were adsorbed. Difficulties in releasing some of the priority pollutants from the activated carbon have been encountered and the recovery percentages for certain priority pollutants are low. It is possible that some of these priority pollutants could be adsorbed on clays and recovered more efficiently than they are from the activated carbon.

External to adsorbing organic pollutants specifically from water and wastewater, but within the realm of sanitary engineering, are several areas where these clays could be utilized. Kerr (76) studied a decontamination method for biologically dangerous radioisotopes produced when uranium is burned in a nuclear reactor. These radioisotopes have such long half-lives that decontamination by tank storage is not feasible. Kerr attempted the retention of such hazardous fission products as Sr, Cs and Ba, without separation from the original reactor waste in fired ceramic masses that subsequently may be buried in pits, mine caves, or other geologically satisfactory places. He found attapulgite clay to show promise in adsorbing the reactor waste. The sinters that were formed by drying, fuming, and firing the mixture did not show significant leaching of beta radiation when exposed to water.

Tamura (126) reported that clay minerals have a vital role in the disposal of radioactive wastes. Illite improved by heat is routinely used in large-scale wastewater treatment operations. Attapulgite has been useful in developing inexpensive mixes for disposal of intermediate-level wastes. Illite has also been found to exhibit a high selectivity for radiocesium.

Tailor made clays may also prove useful as liners at sites where hazardous wastes are stored in liquid form. Although some leaching may occur, it is possible that clays prepared in an appropriate manner could adsorb the hazardous materials from the leachate as it passes through the clay liner.

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APPENDIX A

Organic Compounds Identified in Drinking Water Supplies (1)

1. Acenaphthylene
2. Acetaldehyde
3. Acetic acid
4. Acetone[1]
5. Acetophenone
6. Acetylene dichloride
7. Aldrin
8. Atrazine
9. (Deethyl) atrazine
10. Barbital
11. Behenic acid, methyl ester
12. Benzene[1]
13. Benzene sulfonic acid
14. Benzoic acid
15. Benzopyrene
16. Benzothiazole
17. Benzothiophene
18. Benzyl butyl phthalate
19. Borneol
20. Bromobenzene
21. Bromochlorobenzene
22. Bromodichloromethane
23. Bromoform
24. Bromoform butanal
25. Bromophenyl phenyl ether
26. Butyl benzene
27. Butyl bromide
28. Camphor
29. E-caprolactam
30. Carbon disulfide
31. Carbon tetrachloride
32. Chlordane
33. Chlorobenzene
34. 1, 2-bis-chloroethoxy ethane
35. b-chloroethyl methylether
36. Chloroform[1]
37. Chlorohydroxy benzophenone
38. Bix-chloroisopropyl ether
39. Chloromethyl ether
40. Chloromethyl ethyl ether
41. M-chloronitrobenzene
42. 3-chloropyridine
43. O-cresol
44. DDE

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[1] One of the eleven organic compounds used in this study.

45. DDT
46. Decane
47. Dibromobenzene
48. Dibromochloromethane
49. Dibromodichloroethane
50. Di-t-butyl-p-benzoquinone
51. Dibutyl phthalate
52. 1, 4-dichlorobenzene
53. Dichlorodifluoroethane
54. 1, 2-dichloroethane
55. Dichloroethyl ether
56. Dieldrin
57. Diethyl phthalate
58. Di (2-ethylhexyl) phthalate
59. Dihexyl phthalate
60. Dihydrocarvone
61. Di-isobutyl carbinol
62. Di-isobutyl phthalate
63. 1, 2-dimethoxy benzene
64. 1, 3-dimethyl naphthalene
65. 2, 4-dimethyl phenol
66. Dimethyl phthalate[1]
67. Dimethyl sulfoxide
68. 4, 6-dinitre-2-aminophenol
69. 2, 6-dinitrotoluene
70. Dioctyl adipate
71. Dipropyl phthalate
72. Docosane
73. N-dodecane
74. Eicosane
75. Endrin
76. Ethanol
77. Ethylamine
78. Ethyl benzene
79. 2-ethyl-n-hexane
80. cis-2-ethyl-4-methyl-1, 3-dioxolane
81. Trans-2-ethyl-4-methyl-1, 3-dioxolane
82. O-ethyltoluene
83. Guaiacol
84. Heptachlor
85. Heptachlor epoxide
86. 1, 2, 3, 4, 5, 7, 7-heptachloronorbornene
87. Hexachlorobenzene
88. Hexachloro-1, 3-butadiene
89. Hexachlorocyclohexane
90. Hexachloroethane
91. Hexadecane
92. 2-hydroxyadiponitrile
93. Indene
94. Isodecane

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[1] One of the eleven organic compounds used in this study.

95. Isophorone
96. Isoborneol
97. Isopropenyl-4-isopropyl benzene
98. Isopropyl benzene
99. Limonene
100. Methyl ester of lignoceric acid
101. Methane
102. Methanol
103. 2-methoxy biphenyl
104. Methyl benzoate
105. Methyl benzothiazole
106. Methyl biphenyl
107. 3-methyl butanol
108. Methyl chloride
109. Methyl ethyl ketone
110. 2-methyl-5-ethyl-pyridine
111. Methylindene
112. Methyl naphthalene
113. Methyl palmitate
114. Methyl phenyl carbinol (1-phenylethanol)
115. 2-methylpropanol
116. Methyl stearate
117. Methylene chloride
118. Naphthalene
119. Nitroanisole
120. Nitrobenzene[1]
121. Nonane
122. Octadecane
123. Octane
124. Octyl chloride
125. Pentachlorobiphenyl
126. Pentachlorophenol
127. Pentadecane
128. Pentane
129. Pentanol
130. Phenyl benzoate
131. Phthalic anhydride
132. Propanol
133. Propylamine
134. Propylbenzene
135. 1-terpineol
136. 1, 1, 3, 3-tetrachloroacetone
137. Tetrachlorobiphenyl
138. Tetrachloroethane
139. Tetrachloroethylene
140. Tetradecane
141. Thiomethylbenzothiazole
142. Toluene[1]
143. Trichlorobenzene

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[1] One of the eleven organic compounds used in this study.

144. Trichlorobiphenyl
145. 1, 1, 2-trichloroethane
146. 1, 1, 2-trichloroethylene
147. Trichlorofluoromethane
148. 2, 4, 6-trichlorophenol
149. n-tridecane
150. Trimethyl-trioxo-hexahydro-triazine isomer
151. Triphenyl phosphate
152. n-undecane
153. Vinyl benzene
154. Xylene

Toxic Pollutants for Which Technology-Based Effluent Limitations are Required (50, 75)

1. Acenaphthene
2. Acrolein
3. Acrylonitrile
4. Aldrin/Dieldrin
5. Antimony and compounds
6. Arsenic and compounds
7. Asbestos
8. Benzene[1]
9. Benzidine
10. Beryllium and compounds
11. Cadmium and compounds
12. Carbon tetrachloride
13. Chlordane (technical mixture and metabolites)
14. Chlorinated benzenes (other than dichlorobenzenes)
15. Chlorinated ethanes (including 1, 2-dichloroethane, 1, 1, 1-trichloroethane, and hexachloroethane)
16. Chloroalkyl ethers (chloromethyl, chloroethyl, and mixed ethers)
17. Chlorinated naphthalene
18. Chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)

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[1] One of the eleven organic compounds used in this study.

19. Chloroform[1]
20. 2-Chlorophenol
21. Chronium and compounds
22. Copper and compounds
23. Cyanides
24. DDT and metabolites
25. Dichlorobenzenes (1,2-, 1,3-, and 1,4-dichlorobenzenes)
26. Dichlorobenzidine
27. Dichloroethylenes (1,1- and 1,2-dichloroethylene)
28. 2,4-Dichlorophenol
29. Dichloropropane and dichloropropene
30. 2,4-Dimethylphenol
31. Dinitrotoluene
32. Diphenylhydrazine
33. Endosulfan and metabolites
34. Endrin and metabolites
35. Ethylbenzene
36. Fluoranthene
37. Haloethers (other than those listed elsewhere; includes chlorophenylphenyl esters, bromophenylphenyl ether, bis(dichloroisopropyl) ether, bis(chloroethoxy) methane, and polychlorinated diphenyl ethers)
38. Halomethanes (other than those listed elsewhere; includes methylene chloride, methyl chloride, methyl bromide, bromoform, dichlorobromomethane, trichlorofluoromethane, dichlorodifluoromethane)
39. Heptachlor and metabolites
40. Hexachlorobutadiene
41. Hexachlorocyclohexane (all isomers)
42. Hexachlorocyclopentadiene
43. Isophorone
44. Lead and compounds
45. Mercury and compounds
46. Naphthalene
47. Nickel and compounds
48. Nitrobenzene[1]
49. Nitrophenols (including 2,4-dinitrophenol, dinitrocresol)
50. Nitrosamines
51. Pentachlorophenol
52. Phenol[1]
53. Phthalate esters[1]
54. Polychlorinated biphenyls (PCBs)

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[1] One of the eleven organic compounds used in this study.

55. Polynuclear aromatic hydrocarbons (including benzanthracenes, benzopyrenes, benzofluoranthene, chrysenes, dibenzanthracenes, and indenopyrenes)

56. Selenium and compounds

57. Silver and compounds

58. 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)

59. Tetrachloroethylene

60. Thallium and compounds

61. Toluene[1]

62. Toxaphene

63. Trichloroethylene

64. Vinyl chloride

65. Zinc and compounds

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[1] One of the eleven organic compounds used in this study.

EPA List of "Priority Pollutants" and the Relative Frequency of These Materials in Industrial Wastewaters (75)

Percent of Samples[1]	Number of Industrial Categories[2]		Percent of Samples[1]	Number of Industrial Categories[2]	
31 are purgeable organics					
1.2	5	Acrolein	2.1	5	1,2-Dichloropropane
2.7	10	Acrylonitrile	1.0	5	1,3-Dichloropropene
29.1	25	Benzene[3]	34.2	25	Methylene chloride
29.3	28	Toluene[3]	1.9	6	Methyl chloride
16.7	24	Ethylbenzene	0.1	1	Methyl bromide
7.7	14	Carbon tetrachloride	1.9	12	Bromoform
5.0	10	Chlorobenzene	4.3	17	Dichlorobromomethane
6.5	16	1,2-Dichloroethane	6.8	11	Trichlorofluoromethane
10.2	25	1,1,1-Trichloroethane	0.3	4	Dichlorodifluoromethane
1.4	8	1,1-Dichloroethane	2.5	15	Chlorodibromomethane
7.7	17	1,1-Dichloroethylene	10.2	19	Tetrachloroethylene
1.9	12	1,1,2-Trichloroethane	10.5	21	Trichloroethylene
4.2	13	1,1,2,2-Tetrachloroethane	0.2	2	Vinyl chloride
0.4	2	Chloroethane	7.7	18	1,2-trans-Dichloroethylene
1.5	1	2-Chloroethyl vinyl ether	0.1	2	bis(Chloromethyl) ether
40.2	28	Chloroform[3]			
46 are base/neutral extractable organic compounds					
6.0	9	1,2-Dichlorobenzene	5.7	11	Fluorene
		1,3-Dichlorobenzene	7.2	12	Fluoranthene
		1,4-Dichlorobenzene	5.1	9	Chrysene
0.5	5	Hexachloroethane	7.8	14	Pyrene
0.2	1	Hexachlorobutadiene	10.6	16	Phenanthrene
1.1	7	Hexachlorobenzene			Anthracene
1.0	6	1,2,4-Trichlorobenzene	2.3	6	Benzo(a)anthracene
0.4	3	bis(2-Chloroethoxy)methane	1.6	6	Benzo(b)fluoranthene
10.6	18	Naphthalene	1.8	6	Benzo(k)fluoranthene
0.9	9	2-Chloronaphthalene	3.2	8	Benzo(a)pyrene

1.5	13	Isophorone	0.8	4	Indeno(1,2,3-c,d)pyrene
1.8	9	Nitrobenzene[3]	0.2	4	Dibenzo(a,h)anthracene
1.1	3	2,4-Dinitrotoluene	0.6	7	Benzo(g,h,i)perylene
1.5	9	2,6-Dinitrotoluene	0.1	2	4-Chlorophenyl phenyl ether
0.04	1	4-Bromophenyl phenyl ether	0	0	3,3'-Dichlorobenzidine
41.9	29	bis(2-Ethylhexyl)phthalate	0.2	4	Benzidine
6.4	12	Di-n-octyl phthalate	1.1	4	bis(2-Chloroethyl)ether
5.8	15	Dimethyl phthalate[3]	0.8	7	1,2-Diphenylhydrazine
7.6	20	Diethyl phthalate	0.1	1	Hexachlorocyclopentadiene
18.9	23	Di-n-butyl-phthalate	1.2	5	N-Nitrosodiphenylamine
4.5	12	Acenaphthylene	0.1	1	N-Nitrosodimethylamine
4.2	14	Acenaphthene	0.1	2	N-Nitrosodi-n-propylamine
8.5	13	Butyl benzyl phthalate	1.4	6	bis(2-Chloroisopropyl)ether

11 are acid extractable organic compounds

26.1	25	Phenol[3]	1.9	8	p-Chloro-m-cresol
2.3	11	2-Nitrophenol	2.3	10	2-Chlorophenol
2.2	9	4-Nitrophenol	3.3	12	2,4-Dichlorophenol
1.6	6	2,4-Dinitrophenol	4.6	12	2,4,6-Trichlorophenol
1.1	6	4,6-Dinitro-o-cresol	5.2	15	2,4-Dimethylphenol
6.9	18	Pentachlorophenol			

26 are pesticides/PCB's

0.3	3	α-Endosulfan	0.3	3	Heptachlor
0.4	4	β-Endosulfan	0.1	1	Heptachlor epoxide
0.2	2	Endosulfan sulfate	0.2	4	Chlordane
0.6	4	α-BHC	0.2	2	Toxaphene
0.8	6	β-BHC	0.6	2	Aroclor 1016
0.2	4	δ-BHC	0.5	1	Aroclor 1221

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[1] The percent of samples represents the number of times this compound was found in all samples in which it was analyzed for, divided by the total as of 31 August, 1978. Numbers of samples ranged from 2532 to 2998 with the average being 2617.

[2] A total of 32 industrial categories and subcategories were analyzed for organics and 28 for metals as of 31 August, 1978.

[3] One of the eleven organic compounds used in this study.

EPA List of "Priority Pollutants" and the Relative Frequency of These Materials in Industrial Wastewaters (75)

Percent of Samples[1]	Number of Industrial Categories[2]		Percent of Samples[1]	Number of Industrial Categories[2]	
0.5	3	γ-BHC	0.9	2	Aroclor 1232
0.5	5	Aldrin	0.8	3	Aroclor 1242
0.1	3	Dieldrin	0.6	2	Aroclor 1248
0.04	1	4,4'-DDE	0.6	3	Aroclor 1254
0.1	2	4,4'-DDD	0.5	1	Aroclor 1260
0.2	2	4,4'-DDT	-	-	2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)
0.2	3	Endrin			
0.2	2	Endrin aldehyde			
13 are metals					
18.1	20	Antimony	16.5	20	Mercury
19.9	19	Arsenic	34.7	27	Nickel
14.1	18	Beryllium	18.9	21	Selenium
30.7	25	Cadmium	22.9	25	Silver
53.7	28	Chromium	19.2	19	Thallium
55.5	28	Copper	54.6	28	Zinc
43.8	27	Lead			
Miscellaneous					
33.4	19	Total cyanides	Not available		Asbestos (fibrous)
			Not available		Total phenols

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[1] The percent of samples represents the number of times this compound was found in all samples in which it was analyzed for, divided by the total as of 31 August, 1978. Numbers of samples ranged from 2532 to 2998 with the average being 2617.

[2] A total of 32 industrial categories and subcategories were analyzed for organics and 28 for metals as of 31 August, 1978.

[3] One of the eleven organic compounds used in this study.

Organic Compounds Suspected of Being Formed During the Biological Phase of Wastewater Treatment (1)

1. Acetaldehyde[1]
2. Acetic acid
3. Acetone[1]
4. Acetophenone
5. (deethyl) atrazine
6. Benzene[1]
7. Benzoic acid
8. Borneol
9. Isoborneol
10. Carbon disulfide
11. O-cresol
12. 2,4-dimethyl phenol
13. 2,6-dinitrotoluene
14. Ethanol
15. Ethyl amine
16. Methane
17. Methanol
18. 3-methyl butanal
19. Methyl ethyl ketone
20. Methyl phenyl carbinol
21. 2-methyl propanal
22. Methyl stearate
23. Pentanol
24. Propanol
25. Propylamine
26. 1-terpineol
27. Trimethyl-trioxo-hexahydro-triazine isomer

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[1] One of the eleven organic compounds used in this study.

Organic Compounds Positively Identified in Sewage Treatment Plant Effluents (1)

1. Acetone[1]
2. Methylene chloride
3. Chloroform[1]
4. Trichloroethane
5. Trichloroethylene
6. Tetrachloroethylene
7. Dichlorobenzene
8. Trichlorobenzene
9. DDT
10. Trichlorobiphenyl
11. Tetrachlorobiphenyl
12. Pentachlorobiphenyl
13. Dieldrin
14. Benzene hexachloride
15. DDE
16. Pentachlorophenol
17. Hexachloroethane
18. Toluene[1]
19. Ethyl benzene
20. Indene
21. Benzoic acid
22. Phthalic anhydride
23. O-cresol

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[1] One of the eleven organic compounds used in this study.

APPENDIX B

Sedimentation Procedures for Separating Montmorillonite from Wyoming Bentonite

1. Disperse 420 grams of Wyoming bentonite in 14 liters of distilled water (concentration of 30 grams per liter) using a high-speed mixer (Tekmar Co., Model No. SD45) for two minutes at 10,000 revolutions per minute.
2. Transfer the solution into a glass carboy and allow the contents to settle for seventy-two hours.
3. Decant the supernatant into another glass carboy.
4. Shake the carboy containing the supernatant end-to-end for a few minutes and allow the contents to settle for twenty-four hours.
5. Decant the supernatant into another carboy.
6. Shake this carboy end-to-end for a few minutes and allow the contents to settle for another twenty-four hour period.
7. The settled material in this carboy should be the montmorillonite fraction of the Wyoming bentonite.

APPENDIX C

Procedures for Measuring Cation-Exchange Capacity

1. Weigh out three, 5 gram samples of desiccated clay into three separate fifty milliliter centrifuge tubes.
2. Add 30 milliliters of sodium acetate solution to the tubes.
3. Stopper the tubes with clean rubber stoppers and shake end-to-end for five minutes.
4. Centrifuge the tubes at 200 revolutions per second for five minutes, or until the supernatant liquid is clear.
5. Decant and discard the liquid and repeat the shaking and centrifuging four more times using fresh sodium acetate solution.
6. Add 30 milliliters of ninety-five percent ethanol to the tubes and shake end-to-end for five minutes.
7. Centrifuge the tubes and discard the supernatant liquid.
8. Repeat the ninety-five percent ethanol washing three times.
9. Extract the clay from each tube with three, 30 milliliter portions of ammonium acetate solution and collect the extracts in 100 milliliter graduated flasks.
10. Dilute the combined extracts to 100 milliliters and determine the sodium content of the three combined extracts by flame photometry.

APPENDIX D

Sample Calculations Used to Determine the Montmorillonite and Ammonium Salt Fractions in the Alkylammonium-Montmorillonite Recovered for Washing with Distilled Water

$$\text{Grams of alkylammonium-mont.} = \text{grams of mont.} + \text{grams of ammonium salt adsorbed} \tag{1D}$$

$$\text{Meq. of ammonium salt adsorbed} = \frac{\text{meq of ammonium salt ads.}}{\text{gram of mont.}}\,(\text{grams of mont.}) \tag{2D}$$

$$\text{Grams of ammonium salt ads.} = \left(\frac{\text{meq ammonium salt ads.}}{\text{gram of mont.}}\right)\text{grams of mont.}\left(\frac{\begin{array}{c}\text{0.186 grams of ammonium}\\ \text{salt ads.}\end{array}}{\text{meq of ammonium salt ads.}}\right) \tag{3D}$$

Where: 0.186 grams/meq is the equivalent weight of dodecylammonium salt. Substituting 3D into 1D:

$$\text{Grams of alkylammonium-mont.} = \text{grams of mont.} + \left(\frac{\text{meq of ammonium salt ads}}{\text{Gram of mont.}}\right)$$

$$\text{Factoring out grams of mont.:}\quad \text{grams of mont.}\left(\frac{\text{0.186 grams of ammonium salt ads.}}{\text{meq of ammonium salt ads}}\right) \tag{4D}$$

$$\text{Grams of alkylammonium-mont.} = \text{grams of mont.}\left[1 + \left(\frac{\text{meq ammonium salt ads.}}{\text{gram of mont.}}\right)\frac{\begin{array}{c}\text{0.186 grams of}\\ \text{ammonium salt ads.}\end{array}}{\begin{array}{c}\text{meq of ammonium}\\ \text{salt ads}\end{array}}\right] \tag{5D}$$

Rearranging 5D:

$$\text{grams of mont.} = \frac{\text{grams of alkylammonium-mont.}}{1 + \dfrac{\text{meq ammonium salt ads}}{\text{gram of mont.}}\left(\dfrac{\text{0.186 grams of amm. salt ads.}}{\text{meq of amm. salt ads}}\right)} \tag{6D}$$

Rearranging 1D:

Grams of ammonium salt ads. = g of alkylammonium-mont. - grams of mont. (7D)

Example for a dodecylammonium-montmorillonite sample

Measured weight of dodecylammonium-montmorillonite recovered = 1.9863 grams

Calculated meq of dodecylammonium salt adsorbed per gram of mont. = 1.33 meq/gram

Using 6D:

$$\text{Grams of mont.} = \frac{1.9863}{1 + 1.33\ (0.186)} = 1.592 \text{ grams}$$

Using 7D:

Grams of dodecylammonium salt adsorbed = 1.9863 - 1.592 = 0.394 grams.