

THE ADSORPTION OF WATER AND METHANOL VAPORS
BY ORGANIC COMPLEXES OF MONTMORILLONITES

by

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THE ADSORPTION OF WATER AND METHANOL VAPORS
BY ORGANIC COMPLEXES OF MONTMORILLONITES

INTRODUCTION

Purpose of the Study

This investigation was carried out to determine to what extent the polar molecules of water and methanol would interact with three different amine type organic clay complexes. When a hydrophilic, inorganic, montmorillonite clay is converted to an amine complex, the resultant substance is found to be hydrophobic. It would seem that gas adsorption studies of this hydrophobic product might give some information regarding the nature and extent of this unusual conversion. Therefore, adsorption isotherms, effective surface areas, isosteric heats of adsorption, and heats of immersion have been determined for the two adsorbates, water and methanol, on three montmorillonite complexes.

Origin of Clays

Clay is a popular term for a variety of earthy substances of widely varied origins, of great dissimilarity in their composition and in many of their chemical and physical properties, and differing greatly in almost every conceivable respect. Attempts have been made to

include in the term clay all minerals capable of becoming plastic when moistened or mixed with a suitable quantity of water, but this definition is so wide as to be impracticable, and leads to the inclusion of many substances which have no real connection with clays. A modern definition of clay is more specific. Mineralogically, clay can be defined as that fraction of soil or earth containing the smallest particles; for the geologist this would mean material finer than about 4 microns, for the soil scientist the upper limit of particle size would be 2 microns (34, p. 1).

Clays are always of secondary origin and result primarily from the decomposition of granite and other rocks through weathering or hydrothermal action. Many clays have also been formed by volcanic action. Bentonites were formed in this manner from deposits of volcanic ash. Naturally occurring clays, therefore, usually contain two or more clay types and almost always contain varying percentages of nonclay material.

The Clay Mineral Concept

For centuries, man has recognized the importance of clay in such things as ceramics and agriculture, but little progress was made in the study and clarification of clay materials until 20 or 30 years ago. The early

attempts at the clarification of clay structures were confused by apparent anomalies in the observed physical and chemical properties of the clays under study. Clays that exhibited very similar physical properties were found to have very different chemical compositions, and clays of the same ultimate chemical composition frequently had very different physical attributes. A wide variety of speculative theories was proposed in the older literature to explain these perplexing observations and to describe the structure of clay materials. Only until recently, however, have there been adequate analytical tools to determine with some certainty the fundamental structure of most clay substances.

Primarily through the applications of x-ray diffraction, the fundamental crystalline nature of clays was eventually established (16, p. 2). The first x-ray diffraction analysis of clays was done in 1923. Since then, the x-ray method has been the most widely used means of identification of clays and is of the greatest importance for studying their crystalline characteristics. From this early x-ray work, and the application of the electrostatic valency principle of Pauling, the modern clay mineral concept evolved. The basic tenets of this concept are that clays are essentially composed of extremely small crystalline particles of one or more

members of a small group of minerals which have come to be known as the clay minerals, and that these clay minerals are essentially hydrous aluminum silicates with magnesium or iron proxying for a part of the aluminum in some, and alkali or alkaline earth metals present as essential constituents. Some clays are composed of a single clay mineral but most are mixtures of two or more.

The Laminar Structure of Montmorillonite

Before examining the crystal structure of the montmorillonite group of clay minerals in more detail, it would be helpful to first look at a brief summary of the basic structural units encountered in these substances. The primary arrangement of the silicon ion, as predicted by the electrostatic valence rules, is the tetrahedral structure shown in Figure 1 as the orthosilicate unit. The number and type of atom or group in every lattice plane and the amount of available or needed electrons in every sheet is shown. The four covalent bonds of silicon are distributed tetrahedrally. These four bonds are of equal strength and the arrangement of the four oxygen atoms is symmetrical.

These silica tetrahedra can now hook together in many ways, extending themselves continuously in one, two, or three dimensions or forming a variety of ring

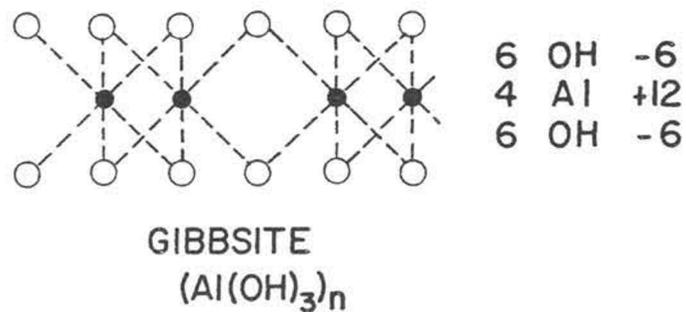
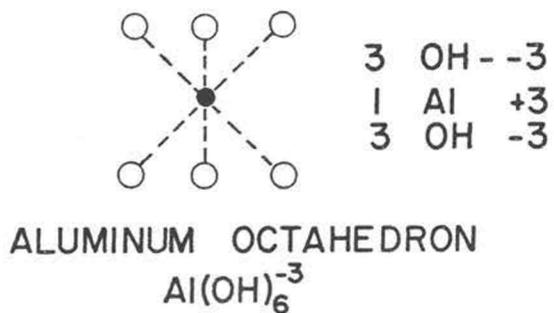
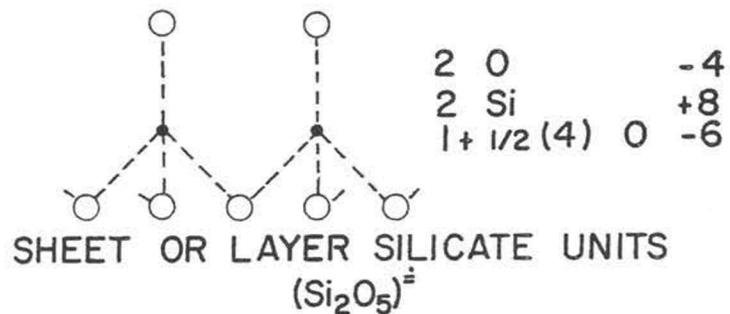
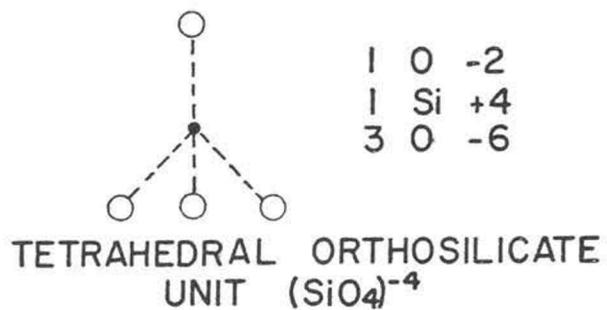


FIGURE I. THE BUILDING BLOCKS FOR MONTMORILLONITE TYPE CLAYS.
ALL ATOMS HAVE BEEN PROJECTED INTO ONE PLANE.

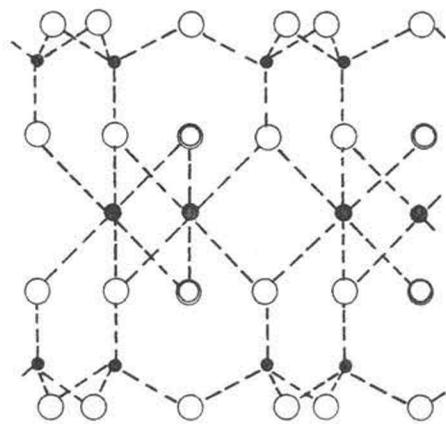
structures. Each possible structure, no matter how complex, will contain the primary silica tetrahedra. The grouping important to building a clay structure is the sheet or layer unit, $(\text{Si}_2\text{O}_5)^{--}$, which is capable of extending itself continuously in two dimensions as is shown in Figure 1.

The other major structural unit of the montmorillonite clays is the alumina octahedra. The arrangement of six groups around an aluminum atom follows the octahedral pattern, also shown in Figure 1. The aluminum unit important to clay structure is that of aluminum hydroxide, $\text{Al}(\text{OH})_3$, in the form of gibbsite. Gibbsite is also a sheet or laminar type of crystal, capable of extending itself continuously in two dimensions.

In the $(\text{Si}_2\text{O}_5)^{--}$ layer silicate unit, it can be seen that the unattached bonds extend in the direction normal to the plane of the layer. If we now think of condensing the gibbsite layer through its hydroxyl groups, bonds can be established from the gibbsite layer to the unattached oxygen atoms of the silicate layer. Upon further condensation of the gibbsite layer, another set of bonds can be established on the other side of the gibbsite layer to the unattached oxygen atoms of a second silicate layer. The final result will be the formation of a three-layer crystal through the establishment of a

Si - O - Al - O - Si type bond system. This leads to the structure of pyrophyllite (Figure 2) as proposed by Pauling (62, p. 123-129). This structure exists in layers, each layer extending continuously in two dimensions and presenting planar surfaces that are populated with oxygen atoms, each attached to two silicon atoms. The oxygen atoms on the exposed surface of the clay are situated in joined hexagonal rings in an arrangement much like the carbon atoms in the graphite crystal. This oxygen-populated face presents an active adsorption surface, and it is this surface which is primarily responsible for the adsorption type complexes to be mentioned later.

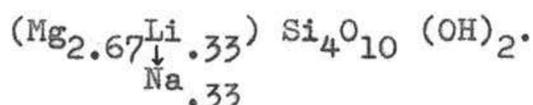
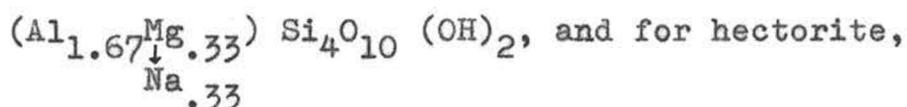
Pyrophyllite can be thought of as the parent compound of the montmorillonite group. Variations within the group arise from isomorphic substitutions within the crystal lattice. These slight modifications lead to considerable differences in the characteristics of these clays. In pyrophyllite itself, no isomorphic substitution is believed to occur. Consequently, it contains no calcium or magnesium, and little or no sodium or other replaceable bases. Water and other polar liquids do not easily wet surfaces of the silicate lamina, with the result that this clay does not swell or expand in these media.



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

FIGURE 2. PYROPHYLLITE. ALL ATOMS HAVE BEEN PROJECTED INTO ONE PLANE.

The various isomorphous substitutions within the montmorillonite group consist mainly of Mg^{+2} replacing Al^{+3} in the octahedral positions, and Al^{+3} replacing Si^{+4} in tetrahedral positions to the extent of one in four. Among varying extents of these replacements are the clay minerals hectorite and bentonite with which this study is concerned. In bentonite, Mg^{+2} replaces some of the Al^{+3} in the octahedral positions, and in hectorite, Li^{+} and Mg^{+2} replace all of the Al^{+3} in the octahedral positions. The formulas of these clay minerals suggested by Ross and Hendricks (65, p. 23-29) are for bentonite,



There is a point of contention regarding the structure of bentonite. The structure originally proposed by Hoffman, Endell and Wilm (45, p. 340-348) has been widely accepted and is the structure that is in accord with Pauling's picture of pyrophyllite. However a contrasting arrangement of the oxygen and hydroxyl groups in the three-layer structure, no longer generally accepted, was submitted by Edelman and Favejee (23, p. 417-431). The major difference is that the Edelman and Favejee structure has every other silica tetrahedron

in both silica sheets inverted, so that half of them point in the opposite direction. Those that point away from the silica sheet have the tip replaced by OH.

Cation-Exchange Capacity

As can be seen from Figure 2, the net electrostatic charge of the unit cell of pyrophyllite is zero. When there is an isomorphic substitution of one ion for another in the clay laminar lattice, the resultant charge must be equivalent to the original charge. Thus, when Al^{+3} is replaced with Mg^{+2} , a net negative charge will exist on the clay lattice. This charge must be counterbalanced by cations in addition to those within the structural framework of the crystal lattice. These cations are located on the exterior of lattice layers and are held by electrostatic attraction. The external ion becomes easily hydrated in aqueous media, and because it occupies no assigned position with respect to the lattice, it may be replaced by other cations. This property of exchangeability is known as cation-exchange, and varies greatly among the clays (50, p. 18). The cation-exchange capacity for clay minerals in the montmorillonite group ranges from about 80 to 150 milliequivalents per 100 grams clay.

These external exchangeable ions, as well as

giving to the clay an ion-exchange capacity, also produce marked differences in characteristics of the various clays. The strong hydrophilic nature of most of these types of clays is due primarily to the ease with which the cations pick up water of hydration. Much work has been done on these hydration reactions. Hendricks, Nelson and Alexander (42, p. 1457-1464) studied the water sorption of a montmorillonite clay as a function of the cation present in the exchange position. Hendricks and Jefferson (41, p. 863-875) found that the interlamellar water of hydrated montmorillonites existed in layers of joined hexagonal nets. They explain this phenomena by considering the expected arrangement of six water molecules around a hydrated cation. The swelling properties of clays arise when successive layers of this interlamellar water build up, pushing apart the individual platelets.

To a limited extent, clays exhibit exchange of anions. These exchanges are usually associated with the edges of the laminar crystal where fluoride, chloride, phosphate, etc. ions may exchange with hydroxyl groups in the lattice. This type of ion-exchange in clays has not received nearly as much study as cation-exchange, and the present state of understanding is not weel advanced.

HISTORY OF ORGANIC COMPLEXES OF MONTMORILLONITES

Types of Organic Complexes

Organic clay complexes can be generally classified in two categories, adsorption complexes and cation-exchange complexes. The first group, as mentioned earlier, arises from the physical adsorption of various organic groups upon the active oxygen populated faces of the clay mineral crystallites. The second group of complexes is a direct result of the cation-exchange capacity of the clay and is formed through actual replacement of the inorganic cation by an organic cation such as an amine.

A few complexes do not seem to fall into either of these categories. Emerson (21, p. 461) reported organo-clay complexes between bentonite and high polymers where only the edge faces of the clay crystals were involved. It was suggested that the polymer links the edge faces of the clay crystals together in a series of hydrogen bonds. Deuel, Huber and Gunthard (19, p. 1799-1802) reported the preparation of phenyl derivatives of montmorillonite where the mode of attachment was neither ion-exchange nor physical adsorption but a direct chemical reaction with the clay lattice. It was suggested

that the phenyl radicals form a silicone type bond of some sort with the montmorillonite lattice. Esterification reactions of the type $RX + \text{clay-M} = MX + \text{clay-R}$ have also received some attention. However, attempts to repeat the syntheses of these alkyl or ester derivatives have not been successful.

Adsorption Complexes

Many nonionic and organic molecules are dipoles. The surfaces of the clay mineral structure are also polar. Hence, associations between clay surfaces and polar molecules in contact with them would be expected. The water molecule is very polar and is by far the most important polar compound sorbed by clay minerals, but it is certainly not the only one. Bradley (15, p. 975-981) studied the interaction of glycols, polyglycols, and polyglycol ethers with the basal plane surfaces of montmorillonite. He found that the organic molecules would displace interlaminar water and that the c-axis spacing of the clay crystal would vary with the organic group. The external inorganic ions were not displaced, however. Based on x-ray diffraction data, it was postulated that the polar organic molecules were held to the clay surface through C-H---O type hydrogen bonds between methylene groups and the oxygen surfaces of the clay. These

observations were independently supported by MacEwan (56, p. 577-578 and 55, p. 349-367). Both investigators pointed out that organic-montmorillonite complexes of this type tend to have a high regularity in c-spacing, giving an integral series of very sharp x-ray reflections. This phenomena was further investigated by Mackenzie (58, p. 368-375) and a method was worked out whereby the x-ray identification of these clay minerals was simplified by the addition of organic substances, usually glycerol or ethylene glycol.

Many other types of adsorption complexes have been studied. Glaeser (26, p. 88-90 and 27, p. 81-108) showed that complexes form with acetone and with a variety of alcohols; Hoffman and Brindley (44, p. 15-29) studied the sorption of a series of nonionic aliphatic compounds from aqueous solutions; and Barrer, Mackenzie and MacLeod (4, p. 1736-1744) showed selective adsorption of a number of n-paraffins by montmorillonite and attapulgite. An interesting series of papers by Greene-Kelly reported complexes formed with pyridine (31, p. 425-430) and with saturated organic chains and rings (32, p. 1281-1286). He observed the interesting phenomena that the sorption complexes of montmorillonite and aromatic molecules have two possible orientations, one with the plane of the ring parallel to the silicate sheet, and the other with the

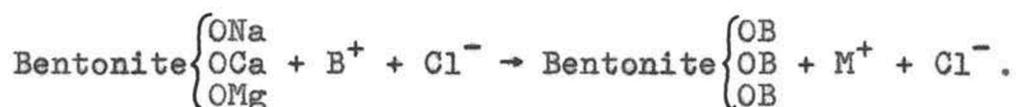
plane of the ring perpendicular to the silicate sheet (30, p. 412-424). The second orientation is only predominant at high surface concentrations of adsorbate.

Cation-Exchange Complexes

Due to the relatively large cation-exchange capacity of montmorillonite, much interest and work has been generated toward cation-exchange complexes. Many common organic cations contain basic amino groups. The reaction between these compounds and clay minerals has been studied in the greatest detail. Some work has been done with other organic compounds, however. Berger (14, p. 42-43), in attempting to elucidate the correct structure of montmorillonite, reported methylated complexes where the methoxyl content was the same as the cation-exchange capacity of the clay. Slabaugh (70, p. 748-751) supposedly synthesized organo-bentonite anhydrides by treatment of the inorganic clay with benzoyl chloride and acetyl chloride in anhydrous media. The clay reaction with amines is, however, the most common and most important.

The first real systematic approach to studying the reactions of clays and organic compounds was by Smith (72, p. 1561-1563). Using amine-like compounds such as nicotine, strychnine, amylamine and hydrazine, he found

that these compounds reacted with the clay in definite stoichiometric ratios. In the process the clay became hydrophobic. He postulated a reaction type;



Giesecking (25, p. 1-13) observed that large, substituted ammonium ions were adsorbed by montmorillonite, giving rise to c-axis spacings greater than those of the inorganic mineral. The adsorbed cations could be replaced by other cations of approximately the same size but they were not replaced readily by the original inorganic ions. The formation of colored compounds of clay was shown to be the result of a reaction between clay and aromatic amines by Hauser and Leggett (39, p. 1811-1814).

In 1941, Hendricks (40, p. 65-81) showed that the cation-exchange capacity exhibited by organic groups was the same as the original inorganic group. Extremely large ions of an effective area greater than 80 square angstroms do not neutralize a hydrogen clay completely however, apparently due to an overlapping of exchange sites. These large ions may be physically adsorbed in excess of the exchange capacity, a phenomenon not observed with smaller ions (35, p. 137-142). This is due to the fact that the organic cations are held to the

surface not only by the coulombic forces due to the ionic nature of the compound but also by van der Waals forces between the molecule and the neighboring surfaces.

The exchange of organic ions on basal plane surfaces has been shown by a shift in the c-axis spacing. An overlapping effect causes this c-axis expansion and was shown most markedly by Jordan (47, p. 294-305). From x-ray data he plotted the c-axis spacing in angstroms versus the chain length of the adsorbed organic molecule. A stepwise separation of the platelets in increments of four angstroms, which is about the van der Waals thickness of a methyl group, indicates that the chains lie flat along the clay laminar surfaces with the planes of the zigzag carbon chains parallel to the plane of the mineral.

Slabaugh (68, p. 162-165) in 1954 and Cowan and White (18, p. 691-697) in 1958 studied in more detail the energies involved in this type of cation-exchange reaction. Slabaugh calculated the equilibrium constants for the reaction;

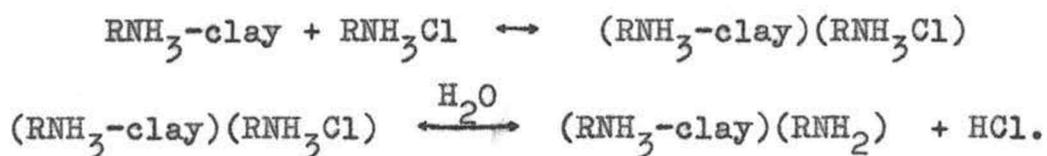


He found that the equilibrium constant K increases as the number of carbon atoms in the R group increases. Cowan and White offered a detailed explanation of

adsorption beyond the cation-exchange capacity. The reaction mechanism postulated has two distinct steps. First, there is an equilibrium between inorganic and organic ions and the clay;



This goes on until all of the sodium ions are replaced. Then the reaction proceeds in the following manner:



When an amine ion exchanges with an inorganic ion on the clay, several factors are concerned; (1) the inorganic ion dissociates from the clay and goes into true solution, (2) the amine ion leaves the solution phase and becomes associated with the colloidal clay particle, (3) the amine ion becomes oriented about the exchange site, its ionic charge balanced by the charge on the clay lamina, and (4) the hydrocarbon chain of the amine adsorbs onto the clay laminar surface, accompanied by the removal of the water which was previously adsorbed on this surface. That is, the hydrophilic laminar surfaces are transformed into hydrophobic surfaces (68, p. 162-165).

This new surface, as well as being hydrophobic,

is also very often organophilic. Greene-Kelly (33, p. 77-79), Stratton (74, p. 76-79) and Jordan (46, p. 598-605) have studied this phenomena with regard to the swelling and gelation properties of the complex in various organic liquids. It was observed that the organophilic properties of the clay complex are negligible until an amine chain length of ten or twelve carbon atoms is reached (47, p. 294-305). The swelling of the clays seemed to be a function of the polarity and dielectric constant of the liquid organic phase.

Barrer et al., in a series of papers from 1955 to the present, have made some very interesting studies of the interlamellar sorption by montmorillonite. In effect, they have held apart the platelets with small alkylammonium groups much like pillars hold up a building. This exposes the interlamellar surfaces to a large variety of organic liquids and sorption selectivity is observed (10, p. 79-89). This immediately suggests the use of this type of substance in chromatographic separations.

Some work has been done on the adsorption of proteins and amino acids on montmorillonite clays. Among those that have carried on investigations of this sort are Ensminger and Giesecking (24, p. 467-473), Talibudeen (75, p. 582-590) and Sieskind and May (66, p. 1652-1655).

Applications

Numerous applications for these organic clay reactions and the resulting complexes are found in the literature. The aromatic amine color reactions can be used for identification and estimation of surface areas, and some study can be made of the structure of the adsorbed cation. Differential thermal analysis of clays treated with organic cations has proved very useful in the study of soil colloids (1, p. 183-188) and methods based on the retention of ethylene glycol have been developed for measuring total surface area, external surface area, and by difference, internal surface area of clays in water and other polar systems (20, p. 421-432). The amine complexes have been incorporated into paints, paint solvents, inks, resins, adhesives, waxes, greases, and general purpose gelling agents (76, p. 1595), and used as reinforcement additives in rubber (49, p. 40-48).

One of the fundamental problems concerning the nitrogen cycle in soil is that of accounting for the great resistance of soil protein to microbial attack. One hypothesis that has been advanced is that protein is protected by adsorption into and on clay mineral particles (60, p. 239-244). Some work has been done using bentonites as testing and adsorption agents (53, p. 207-

211 and 63, p. 234-237) in biochemical research where the activity of the clay depends upon its ability to form organic-type complexes.

In the words of Hauser (38, p. 431-441), "the development of organophilic clays by base-exchange reactions, ... , can very well be considered as a new bridge between inorganic and organic matter. It also offers further proof that colloid chemistry is primarily the chemistry of matter characterized by a high surface-over-volume ratio and that the reactivity of substances present in this state is controlled by the composition of its surface."

THEORETICAL BACKGROUND

Types of Adsorption

Adsorption can be defined generally as that phenomenon which results in a concentration or accumulation of substances at surfaces or interfaces. This may involve two rather distinct types of interactions. The first, called chemisorption, is due to the primary valence forces of the interacting substances and is largely independent of the physical character of the adsorbent. It is a chemical reaction and generally involves a large evolution of heat.

The second more general type is called physical adsorption and arises from physical forces between adsorbent and adsorbate. These forces are of the van der Waals type. Physical adsorption can be considered as an act of condensation of a gas upon the surface of a solid and involves a rather low evolution of heat, in the range of the heat of liquefaction. The most general method of distinguishing between physical adsorption and chemisorption is through the measurement of this heat evolution, although in some cases a clear cut division is not possible. This investigation is involved with physical or van der Waals adsorption of gases on solids.

Theories of Adsorption

Ever since the observation of Scheele in 1773 on the adsorption of gases by charcoal, there have been attempts to derive a theoretical basis for the phenomena. One of the oldest attempted explanations is the empirical expression of Freundlich. In 1915, Langmuir (52, p. 1139-1167) proposed a theory which was based on the belief that adsorption was a type of chemical combination or process and that the adsorbed layer was unimolecular. He obtained experimental verification of his theory from a series of determinations on the adsorption of gases at low pressures on plane surfaces such as mica and glass. When experimental evidence for adsorption in layers more than one molecule thick began to mount, attempts were made to modify Langmuir's equation to fit multi-layer adsorption.

Brunauer, Emmett and Teller (17, p. 309-319) in 1938 derived an isotherm equation for multimolecular layers from data obtained from low temperature gas adsorption on an iron synthetic ammonia catalyst. It is very similar to Langmuir's equation for unimolecular layers, and they soon adopted its use for a very wide range of adsorbents and adsorbates. Emmett, Brunauer and Love (22, p. 57-65) reported its use for measuring

the surface area of soils and soil colloids the same year the theory was first proposed. The major assumption in the Brunauer, Emmett and Teller (B.E.T.) theory is that the same forces that produce condensation are also responsible for multimolecular adsorption. The derivation of the B.E.T. equation results in the following expression for the formation of a monolayer:

$$P/V(P_0 - P) = (1/V_m C) - [(C-1)/V_m C] (P/P_0)$$

where P is the measured pressure, P_0 the saturation pressure, V the volume adsorbed at pressure P , V_m the volume adsorbed on a monolayer, and C a constant related to the heat of adsorption.

If a plot of $P/V(P_0 - P)$ vs P/P_0 is made from experimentally obtained values, a straight line is obtained for values of P/P_0 from 0.05 to 0.35 for a system that conforms to the B.E.T. theory. It can now be seen from the above equation that the slope of this line is $(C-1)/V_m C$ and the intercept on the ordinate is $1/V_m C$. Two equations can be set up with two unknowns and solved for V_m , which gives:

$$V_m = 1/\text{intercept} \times \text{slope}$$

With a value for V_m , the surface area covered by a monolayer can be readily calculated provided the

cross-sectional area of the adsorbed molecule is known. This area is usually found from the known density of the liquified or solidified adsorbate. Thus, the B.E.T. theory provides an absolute method for determining the surface area of a solid, and is still the most widely accepted method for measuring surface areas from gas adsorption data.

An alternate method for determining the area of a solid from adsorption isotherms has been offered by Harkins and Jura (37, p. 1366-1373). In their development, there is no need to assume a molecular area of the adsorbate, which in some cases may be uncertain. The two methods show remarkable agreement, however. This speaks well for both theories, since they are based on two entirely different principals, the B.E.T. method being based on a kinetic theory and the Harkins-Jura method on a thermodynamic theory.

Hysteresis

Theoretically, adsorption-desorption curves should coincide; in practice, they do not, and the resulting phenomenon is termed hysteresis. No explanation has yet been proposed that fits all experimental data, and it is probably correct to say that hysteresis can be caused by several different factors, one or all of which

may be applicable to a specific system. The explanation generally attributed for it is capillary condensation. The capillaries fill by multilayer adsorption, but once filled they desorb by evaporation from a meniscus. The lowering of the vapor pressure associated with a meniscus of a very small radius is the cause for the hysteresis loop. Pierce and Smith (64, p. 784-794), however, have pointed out that hysteresis can be caused by condensation and evaporation effects without the presence of capillaries. They claim that hysteresis is found when adsorption occurs by merging of clumps of molecules on separate sites of a plane surface. After the clumps merge, all molecules are held by forces from all active sites touched by the merged group. Forces are therefore stronger than when the groups were separate, the vapor pressures of all molecules are lowered and there is desorption hysteresis.

The second widely accepted theory to explain hysteresis postulates structural changes within the framework of the adsorbent. This could involve some sort of rearrangement of a crystal lattice due to interaction with the adsorbate, change in particle size or aggregation, and swelling effects. Hirst (43, p. 22-28) attempted to construct models to explain the various forms of hysteresis. He states that if there are regions

within a swelling solid where the surfaces are sufficiently close together for surface forces to contribute appreciably to the cohesion of the solid it can be predicted from a mechanical picture of the model that the isotherm will show hysteresis. This could be the cause of hysteresis in a swelling laminar structure such as an inorganic montmorillonite-water system.

Isosteric Heats of Adsorption and Heats of Immersion

The adsorption of gases by a solid is always accompanied by an evolution of heat. As has been pointed out, the extent of this evolution for physical adsorption is relatively small, being in the range of the heat of liquifaction of the gases taken up. This evolution can be determined in two separate ways. It can be measured calorimetrically as the adsorption takes place or it may be calculated from the resulting isotherms. The calculated or isosteric heats of adsorption depend upon the pressures at different temperatures corresponding to constant amounts adsorbed. With this isotherm data, ΔH can be calculated from the integrated form of the Clausius-Clapeyron equation:

$$dP/dT = P \Delta H/RT^2 \quad \text{or} \quad d \ln P/dT = \Delta H/RT^2$$

upon integration,

$$\log P_2/P_1 = \Delta H (T_2 - T_1) / 2.303 R(T_2 T_1)$$

or

$$\Delta H = 2.303 R(T_2 T_1) / (T_2 - T_1) \log P_2/P_1$$

The theoretical basis for such a calculation has undergone much discussion. Hansen (36, p. 411-415) has claimed that the derivative, dP/dT , should be evaluated at constant A , which he defines as the total surface area of the solid divided by the number of moles of surface excess, instead of at constant amount adsorbed. The former method, however, seems to be the standard accepted procedure.

The energies involved in wetting surfaces can be correlated to isosteric heats. Three wetting processes are possible, adhesional wetting, spreading wetting, and immersional wetting (77, p. 76-81). Immersional wetting results when a solid is immersed in a liquid, forming a liquid-solid interface from the original solid surface. The energy change associated with this wetting process is termed the heat of immersion. For finely divided powders it may be measured calorimetrically by breaking an evacuated glass bulb, containing the powder, while it is immersed in the liquid contained in a calorimeter. This heat of immersion is related to the area under the

plot of isosteric heats versus amount adsorbed, as it involves the energy for total wetting of the surface, a phenomenon described in increments by an adsorption isotherm.

EXPERIMENTAL METHODS AND APPARATUS

Description of Apparatus

The adsorption isotherms were determined gravimetrically on an adsorption balance of the type first described by McBain and Bakr (59, p. 690-695). It is shown diagrammatically in Figure 3. Two reservoirs, one for liquid storage and one for gas storage, are located on the main manifold for easy adsorbate addition. The manifold is fitted with the standard pressure measuring devices: a mercury manometer, an oil manometer filled with Dow Corning 703 fluid, and a McLeod gauge. A second manifold was connected to this main manifold, and the eight adsorption columns were tapped from it, each fitted with an individual stopcock so they could be isolated from the system.

The springs used were small, quartz helixes, each with a sensitivity of about one millimeter extension per milligram. The samples were contained in small buckets made from 0.0005 inch tin foil and fitted with handles made from 0.0056 inch diameter beryllium-copper wire. These buckets were suspended from the quartz helixes by fine glass extension rods which contained coded colored markings for measurement purposes. The bulk of the adsorption columns, containing the springs, was enclosed

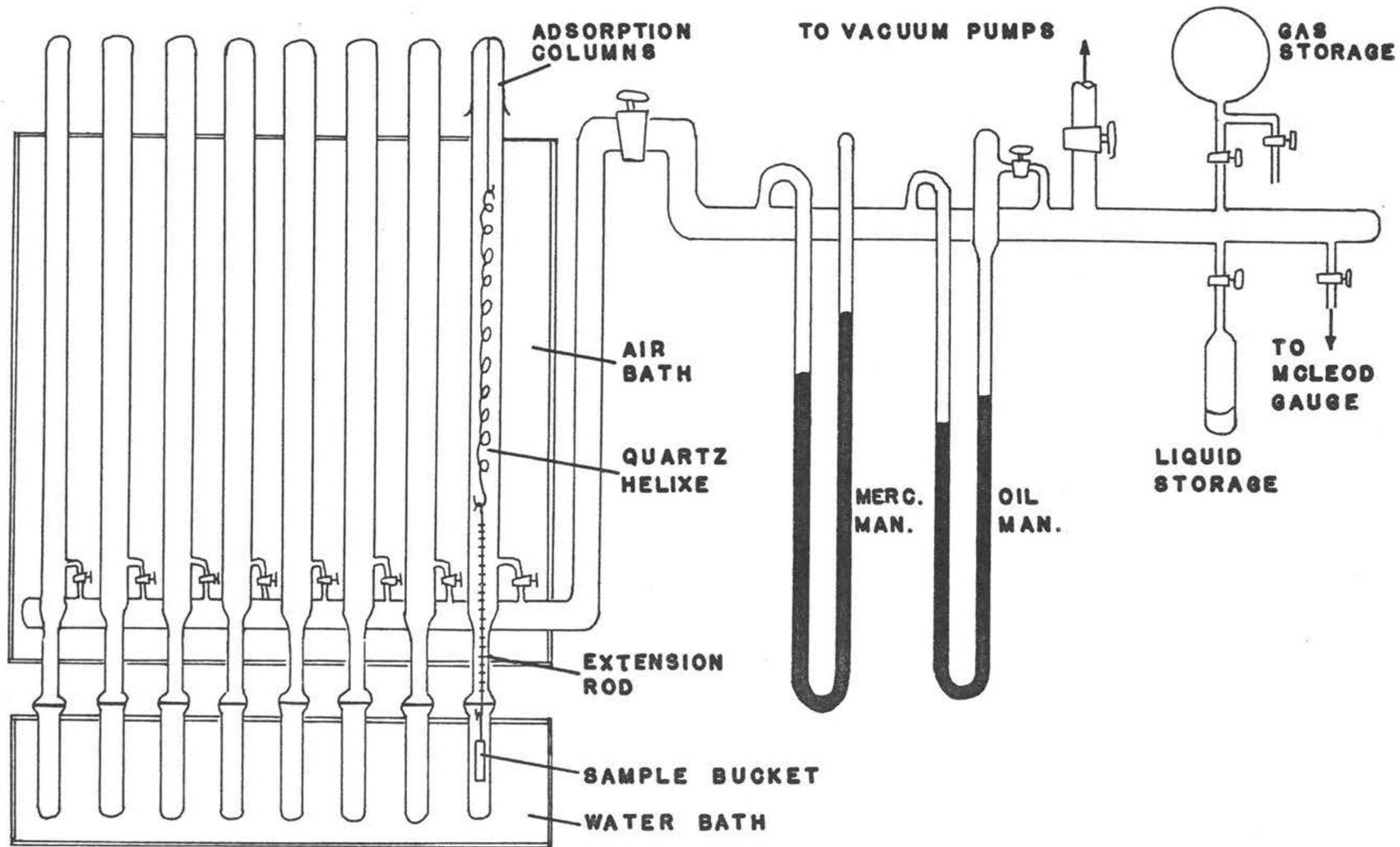


FIGURE 3 GRAVIMETRIC ADSORPTION BALANCE

in a constant temperature air bath maintained at $28.0 \pm 0.5^\circ\text{C}$. The lower portion of the adsorption columns enclosing the sample buckets was kept in a constant temperature water bath for runs near room temperature, and was maintained within $\pm 0.1^\circ$. For low temperature nitrogen runs, this water bath was replaced by Dewar flasks containing liquid nitrogen, the temperature being determined from a vapor pressure thermometer charged with argon.

The spring extensions were magnified by optically projecting the coded markings of the extension rods upon a wall chart about seven feet in front of the sample tubes. The extensions were read out in scale divisions. Each spring was calibrated by adding known weights, and a spring constant was calculated in milligrams per scale division. The sensitivity of the extension readings was about 0.8 milligram per scale division and the scale could be read to 0.05 divisions for an overall sensitivity of ± 0.04 milligram for a 400 milligram sample.

The calorimeter used to determine the heats of immersion has previously been reported by Slabaugh (69, p. 1022-1024). The essential component is the calorimeter head, which contains five sample bulb holders, a breaking device, a stirrer, a detecting thermistor, and a calibration heating coil. The entire head fits into

a widemouth pint Dewar flask which contains the immersing liquid, and this in turn is suspended in an air bath. The air bath was thermostated at $29.0 \pm 0.1^{\circ}\text{C}.$, which holds the internal part of the calorimeter to a constant drift of no more than 0.0001° per minute. A galvanometer serves as the read out device by detecting the off-balance of a Mueller resistance bridge caused by the temperature change in the thermistor. The overall sensitivity of this system permitted the observation of temperature changes in the order of $0.00002^{\circ}\text{C}.$

Preparation of Samples

The adsorbents used in this investigation were three commercially prepared organic-clay complexes of montmorillonite type clays. They were supplied by the Baroid Division of the National Lead Company. The compositions of the complexes were as follows:

Sample 1 - coconut fatty amine bentonite

Sample 2 - dimethyl dioctadecyl ammonium bentonite

Sample 3 - dimethyl dioctadecyl ammonium hectorite

These are all quaternary amine compounds. The coconut fatty amine in sample 1 is a mixture that has approximately 18 carbons per amine group. The amine groups of samples 2 and 3 each contain 38 carbons. In the synthesis of these complexes, stoichiometric quantities were

used. One hundred milliequivalents of the quaternary amine salt was added to 100 grams of clay. This is approximately the cation-exchange capacity of the original clay mineral.

Six separate samples were used. They consisted of the original three clay complexes as they were received from Baroid Division, and designated 1-A, 2-A and 3-A, and three other samples identical to these except that they were pretreated in the laboratory. These latter three are designated 1-B, 2-B and 3-B. This treatment involved extensive extraction with reagent grade isopropyl alcohol in a Soxhlet extractor, subsequent drying in a vacuum oven at 50-60°C. at less than 4 centimeters Hg, and grinding to 200 mesh after which they were again vacuum dried for 16 hours. The extraction apparently removed most of the untreated physically adsorbed amine and other soluble material. Vacuum drying was resorted to after ordinary oven drying was found to leave the clay in very hard lumps, making the grinding process very difficult. All samples were stored at 51% humidity over a saturated solution of calcium nitrate.

The weight of sample used in the calculations of the isotherms was the vacuum dry weight. This was obtained by the application of a correction factor to the wet 51% humidity weights. This correction factor was

calculated independently of the isotherms by outgassing samples at less than one micron pressure for 48 hours, then rapidly weighing them before they had an opportunity to adsorb moisture from the atmosphere.

Procedure

Adsorption isotherms were determined for water and methanol vapor and for comparison, nitrogen at low temperature. The samples were weighed into the tin foil buckets. Sample weight used was about 300 milligrams; the buckets weighed approximately 100 milligrams each for an overall weight of 400 milligrams. The samples were then suspended from the extension rods and sealed into the system. They were outgassed for 48 hours at room temperature. Care had to be taken when pulling the initial vacuum as the powdered samples tended to bump, due to trapped gases in the bucket.

When the samples were completely outgassed, a zero reading was taken on the wall chart. The adsorption isotherm was then determined. Small increments of gas were admitted to the system and allowed to equilibrate. A check on the equilibrium time showed that water and methanol needed about six to eight hours and nitrogen needed only about fifteen minutes to reach equilibrium. Consequently, twelve hour intervals between points were

allowed for both water and methanol and one hour intervals for nitrogen. When the system had equilibrated, the pressure was noted and the spring extension marked on the wall chart. This procedure was repeated throughout the entire isotherm, about ten or twelve points being determined during a run.

Isotherms were determined at 20° and 37°C. for water and methanol so that isosteric heats of adsorption could be calculated, and one desorption run was made for the two adsorbates at 20°. Each adsorption run was repeated to test the reproducibility of the measurements. The major difficulty encountered was in maintaining a tightly sealed vacuum system. It was checked before and after each run, and if there were indications that a leak had developed during the course of a run the data were discarded.

Accurate pressure readings presented some problems, especially with water whose saturation pressure near room temperature is quite small. The oil manometer was used in part of the study, giving a pressure magnification of 12.4 with respect to a mercury manometer. Another method used later which seemed to give more satisfactory results, was an optical system whereby the mercury manometer was projected on a screen about 17 feet away. This gave an overall magnification factor of 25,

and the pressure could easily be read to ± 0.05 millimeter Hg.

The samples for the heats of immersion runs were weighed out in four inch glass tubes that had a constriction in the middle. These were made from eight millimeter pyrex tubing. Each tube contained 200 milligrams of clay. After the clay was placed in the lower portion of the tubes, they were sealed in racks onto the vacuum system and outgassed at room temperature for 48 hours. They were then sealed off at the constriction, producing evacuated sample tubes about two inches long. Several tubes for each type clay-complex were outgassed an additional 2 hours at 100°C . to test the efficiency of outgassing at room temperature. The tubes were then scratched to facilitate breaking and mounted in the tube holders of the calorimeter head and immersed in the liquid. When the calorimeter had reached equilibrium, the constant drift of the galvanometer was noted and a tube was broken. Galvanometer deflections were recorded at thirty second intervals until the constant drift was re-established. The total deflection due to breaking the tube and immersing the sample was then determined by extrapolating both drift curves through the point where the breaking occurred and reading the difference between them at this point. This procedure was repeated until all

sample tubes in the calorimeter were broken. A calibration curve was then made by allowing a known current to pass through a fine heater wire of known resistance. The exact time of current flow was determined by an accurate stopwatch so the amount of heat passing into the calorimeter was readily calculated. This calibration curve was determined for each set of samples run.

EXPERIMENTAL RESULTS AND CALCULATIONS

Adsorption Isotherms and Surface Areas

Water and methanol adsorption on the clay complexes showed the typical type II inverted S-shaped isotherms demonstrated by Figures 4 and 5 for adsorption at 20°C. The data from two separate adsorption runs in each case demonstrates good reproducibility, well within experimental error. The adsorption-desorption curves showed hysteresis throughout the entire pressure range in all cases. The most severe hysteresis was with water vapor on samples 1-A and 1-B, the 18 carbon amine complex, while samples 2-A, 2-B, 3-A and 3-B showed about the same hysteresis loop. The hysteresis effect with methanol was approximately the same for all samples.

B.E.T. plots for water and methanol adsorption at 20° are shown in Figures 6 and 7. The plots for water adsorption show very good linearity between the limits of 0.10 to 0.35 relative pressure. For methanol, the straight line portion of the plot is somewhat longer, extending from 0.10 to about 0.45 relative pressure. These B.E.T. plots were used to calculate W_m , the weight adsorbed on a B.E.T. monolayer in milligrams adsorbed per gram of sample. From these W_m values, effective surface areas were readily calculated using 10.6 and 14.1 square

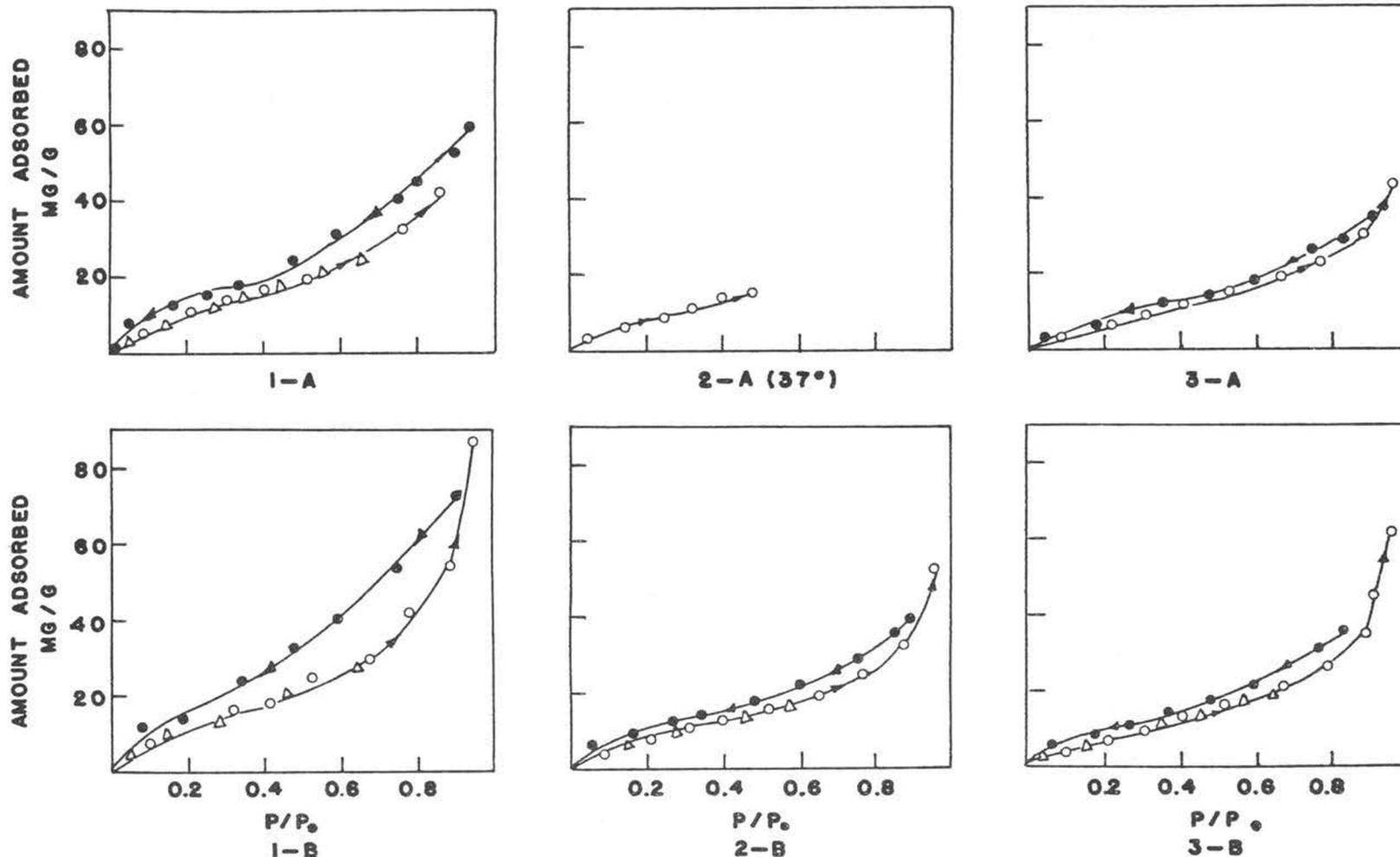


FIGURE 4 WATER ISOTHERMS OF ORGANIC CLAY COMPLEXES AT 20°C

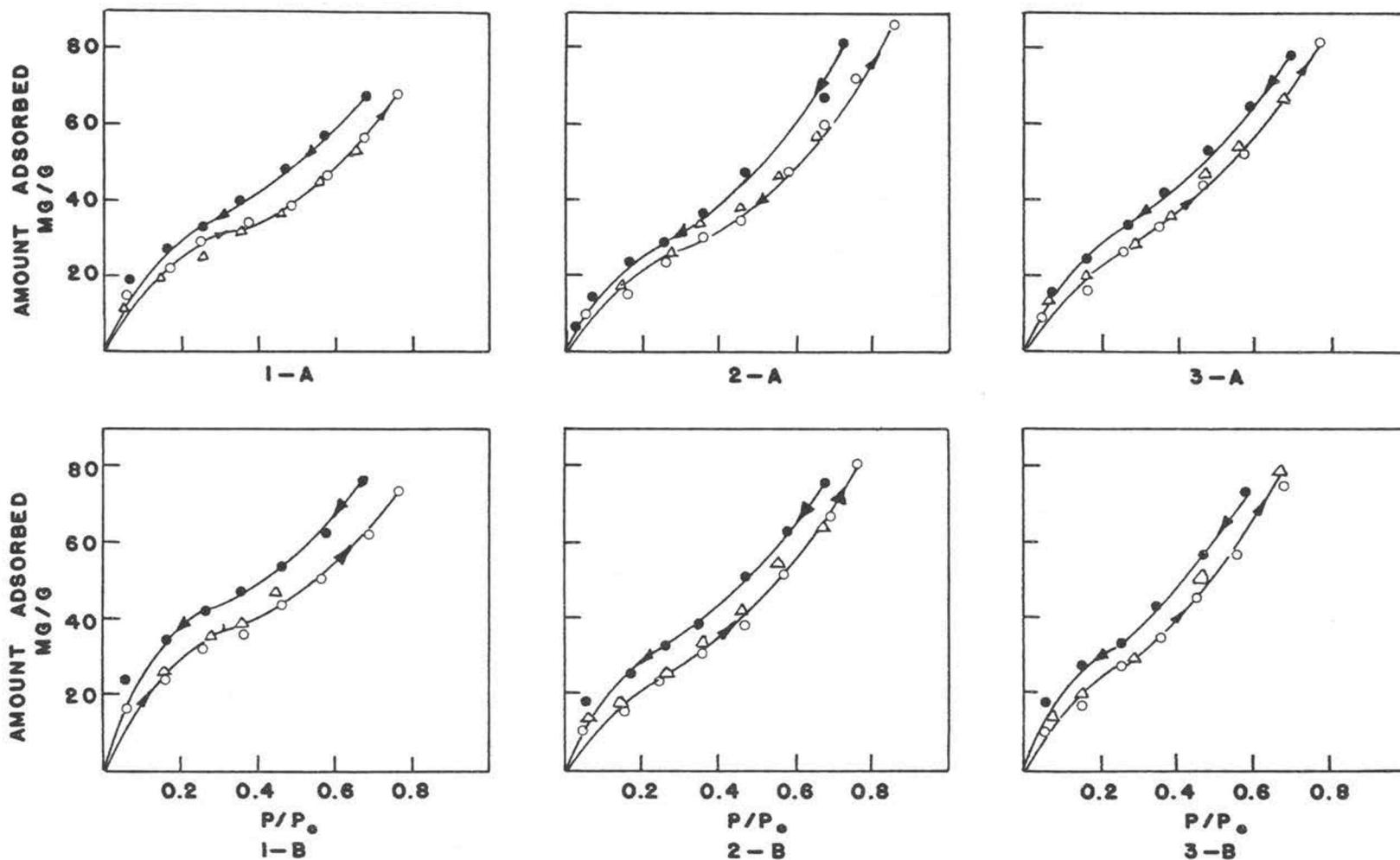


FIGURE 5 METHANOL ISOTHERMS OF ORGANIC CLAY COMPLEXES AT 20°C

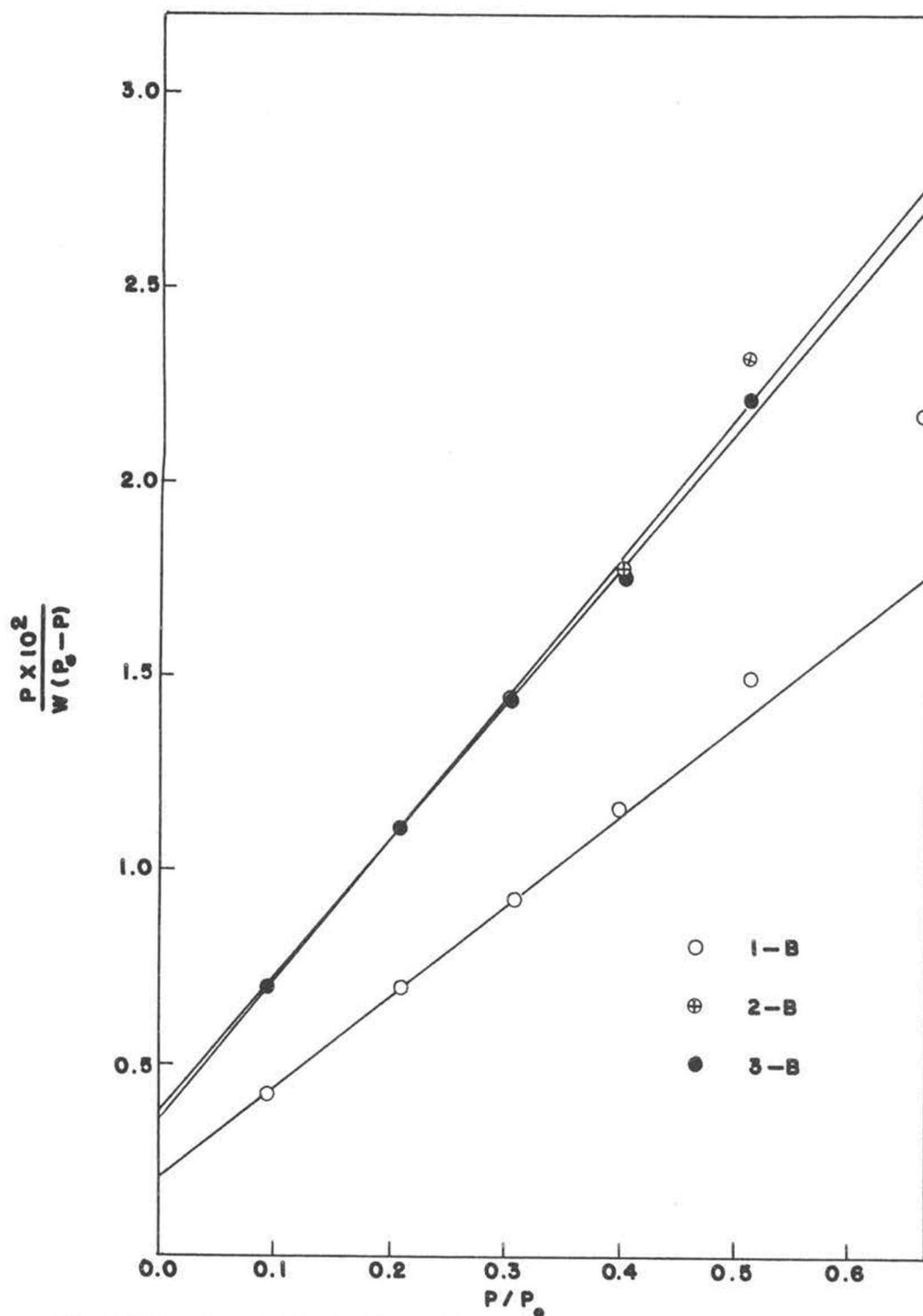


FIGURE 6 B.E.T. PLOTS OF ADSORPTION OF WATER ON ORGANIC CLAY COMPLEXES AT 20°C

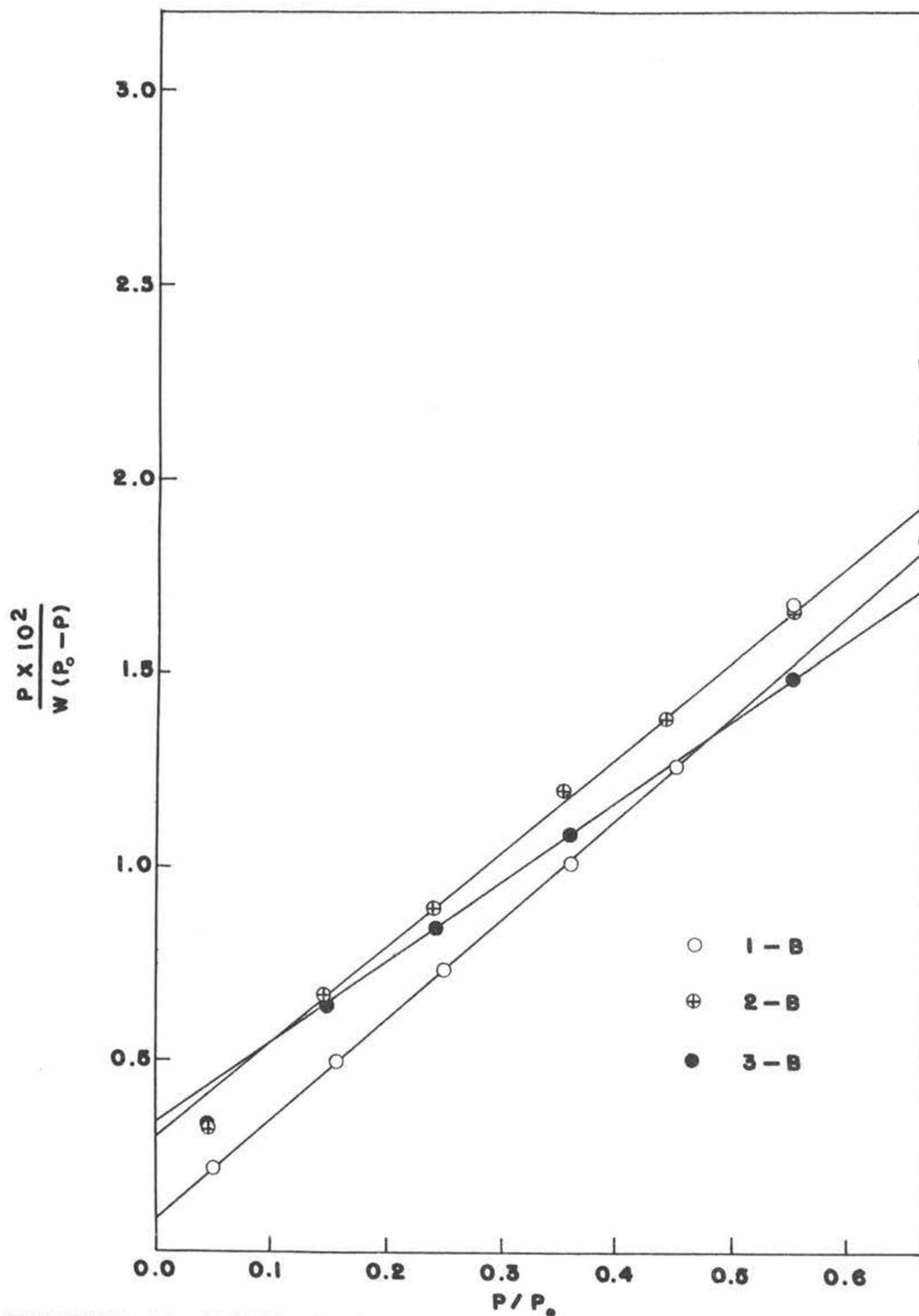


FIGURE 7 B.E.T. PLOTS OF ADSORPTION OF METHANOL ON ORGANIC CLAY COMPLEXES AT 20° C

angstroms for the cross-sectional areas occupied by a water molecule and a methanol molecule, respectively. The results of these calculations are summarized in Table 1. Average values for all runs at 20° are given.

Table 1
Effective Surface Areas
of Organic Clay Complexes

Sample	W_m for Water mg/g	Effective Surface Area m^2/g	W_m for Methanol mg/g	Effective Surface Area m^2/g
1-A	10.9	38.6	22.3	59.1
2-A	8.9 (37°)	31.6 (37°)	23.6	62.6
3-A	8.8	31.2	27.0	71.5
1-B	12.6	44.6	26.1	69.1
2-B	8.6	30.6	24.6	65.2
3-B	8.5	30.3	29.1	77.1

Data for water adsorption on sample 2-A, the unextracted 38 carbon amine bentonite, are given at 37° because no run was made at 20°. The values should be very nearly identical to those for 20° as comparison of values at the two temperatures for the other samples showed complete agreement within the error between individual runs at the same temperature. The variation in

W_m between runs ranged from 0.2 milligram per gram or 2.3% of the average value for sample 2-B to 0.7 milligram per gram or 5.5% for sample 1-B with water vapor, and 0.4 milligram per gram or 1.7% for sample 2-A to 1.9 milligram per gram or 7.3% for sample 1-B with methanol vapor. The areas calculated from the B.E.T. plots are referred to as effective surface areas as they do not necessarily correspond to an actual area, but are the areas occupied by a certain amount of adsorbent, all of which is adsorbed in very nearly the same manner.

Nitrogen adsorption isotherms were determined at -194.7°C and the B.E.T. surface areas calculated for comparison, using 16.2 square anstroms as the cross-sectional area of a nitrogen molecule. W_m values for the extracted samples were 2.07, 3.50 and 3.18 milligrams per gram for samples 1-B, 2-B and 3-B, respectively, indicating much less uptake of nitrogen than of water or methanol. The corresponding surface areas were 7.2, 12.2 and 11.1 square meters per gram. Values for the unextracted samples were still smaller, approaching the limit of sensitivity of the adsorption balance.

Isosteric Heats of Adsorption and Heats of Immersion

A complete set of adsorption isotherms were also obtained at 37°C and the same degree of reproducibility

was observed. Data from these isotherms in conjunction with data from the 20° isotherms were used to calculate isosteric heats of adsorption from the integrated form of the Clausius-Clapeyron equation. The results of these calculations are presented diagrammatically in Figures 8 and 9. Only the isosteric heats of adsorption for the extracted samples were calculated and the data were plotted as ΔH , in kilocalories per mole of adsorbed vapor, versus the fraction of a monolayer formed, W/W_m . Particular attention should be paid to the relation of the ΔH values to those corresponding to the heat of liquifaction of the adsorbate, shown by the dotted line. The apparent anomaly between the curve for water vapor on sample 1-B and the rest of the water vapor curves can be somewhat discredited if the first three points are not considered. These points were calculated from the portion of the isotherms that lie very close together, greatly increasing the chances for error. Such curves demonstrating an initial rise instead of an initial fall in the heat of adsorption have been observed before, but a satisfactory explanation is rather difficult.

The heat of immersion, for each sample, was determined for both water and methanol calorimetrically and the data calculated as calories of heat evolved per gram of clay. The average value for these heats of immersion

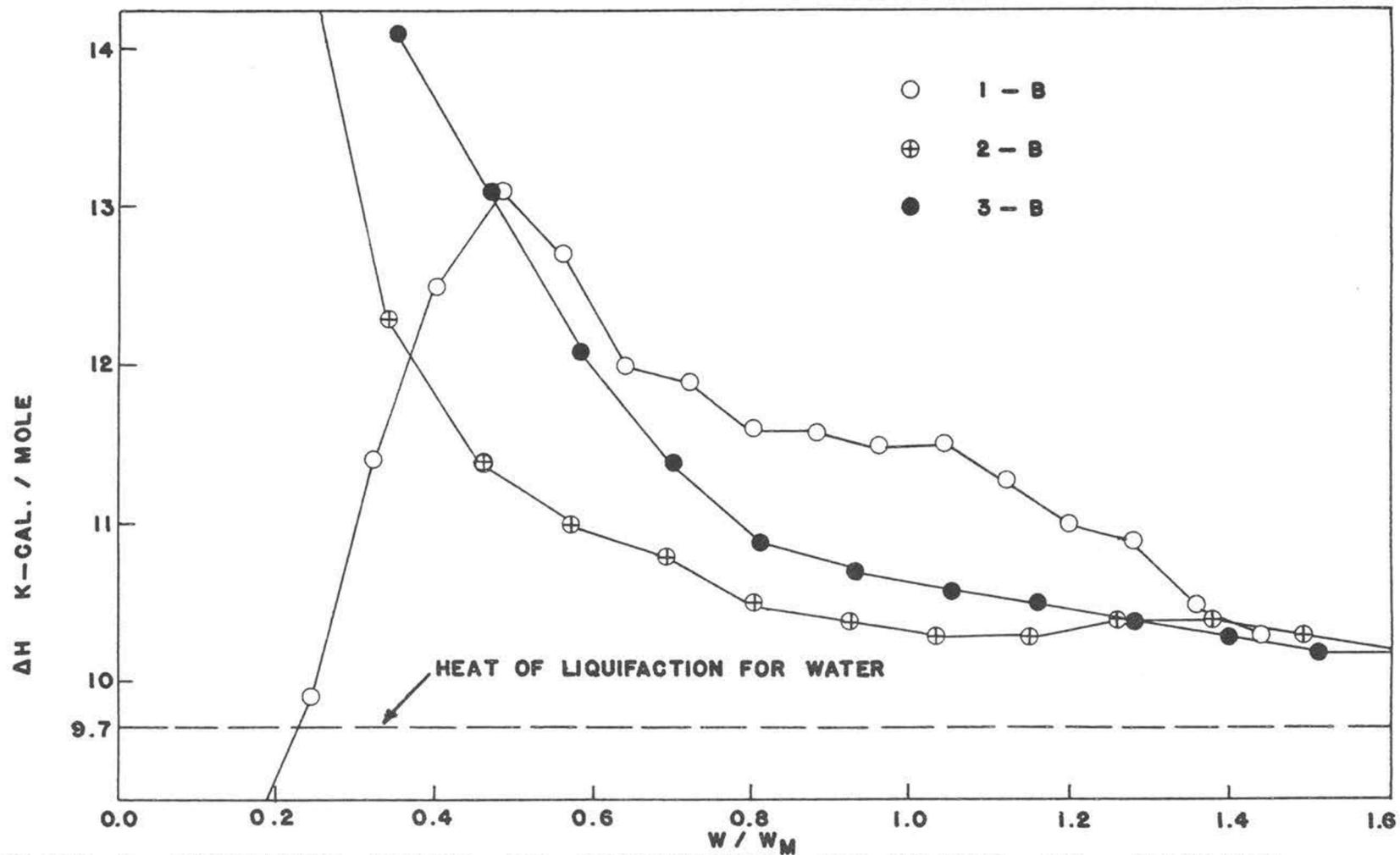


FIGURE 8 ISOSTERIC HEATS OF ADSORPTION OF WATER ON ORGANIC CLAY COMPLEXES

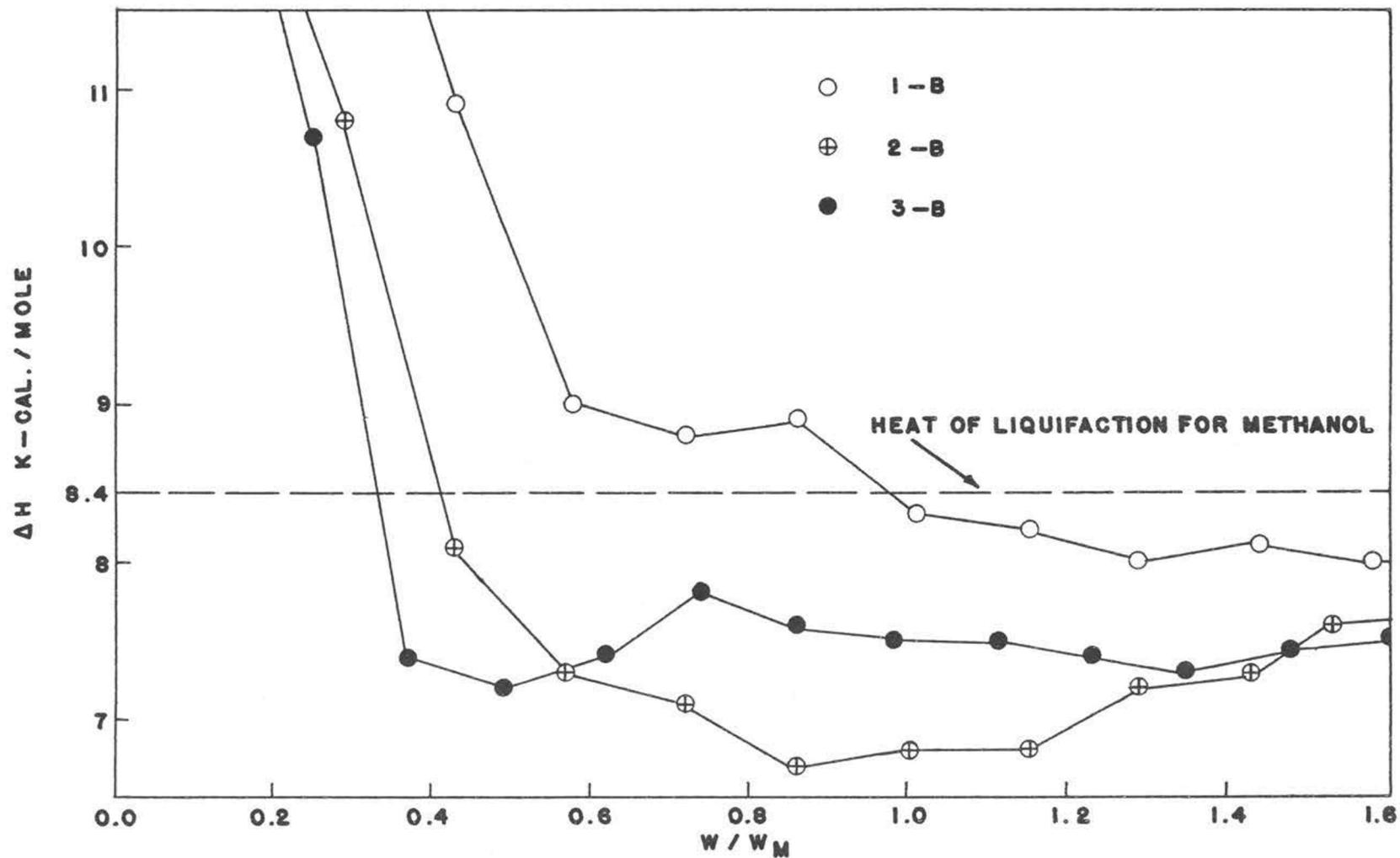


FIGURE 9 ISOSTERIC HEATS OF ADSORPTION OF METHANOL ON ORGANIC CLAY COMPLEXES

is summarized in Table 2. Samples outgassed at 100°C show slightly higher values.

Table 2

Heats of Immersion of Organic Clay Complexes

Sample	Heat of Immersion in Water, Samples Outgassed at Room Temp.	Heat of Immersion Water 100°	Heat of Immersion in Methanol, Samples Outgassed at Room Temp.
	cal/g	cal/g	cal/g
1-A	1.8	2.2	1.1
2-A	-0.05	0.08	-3.3
3-A	0.0	0.53	-3.3
1-B	2.8	3.6	3.3
2-B	0.53	0.86	-2.4
3-B	0.57	1.1	-1.1

A correction factor for the heat involved in breaking and wetting the evacuated sample tubes was not applied since the heat of immersion data showed wide scatter and large errors due to the relatively small heats involved. The data should be considered only in a qualitative way. The relation between values for different samples should be valid.

DISCUSSION

Effective Surface Areas

The values for the surface areas obtained from nitrogen isotherms are in the range usually attributed to the external area of the montmorillonite clays (61, p. 285-296). If these values are assumed to be the external areas of the organic clay complexes, some mechanism must be proposed to explain the higher values obtained with water and methanol isotherms. Indeed, some penetration between the lamina seems to be taking place, but not to a very great extent as the overall surface area of montmorillonite clays is generally attributed to be in the range of 800 square anstroms per gram of clay.

In the case of water adsorption, for sample 1-B, the 18 carbon amine complex, the adsorption takes place over approximately six times the external nitrogen area, while for samples 2-B and 3-B, the longer 38 carbon amine complexes, the excess is only three times the external area. If, for sample 1-B, the chain is thought to extend out from the exchange site, it will have to lap over other chains on neighboring sites due to its length. X-ray work by Jordan, Hook and Finlayson (48, p. 1196-1208) has shown this complex to have two layers of amine

between platelets. But since the chains extend linearly, in a zig-zag fashion, packing efficiency would be very poor and open spaces would exist on the platelet surface. These open spaces would still be active adsorption sites and could explain the water adsorption in excess of the external area for the hydrophobic clay complex. The overlap of amine chains causes a separation of the lamina in the order of four angstroms. The resulting channels would thus be sufficiently large to allow entry of a water molecule.

The 38 carbon amine consists of two 18 carbon chains and two methyl groups attached to a nitrogen atom. Since here two chains radiate out from each exchange site, packing efficiency would be somewhat greater but there would still be some free spaces. Overlapping would occur to an even greater extent. The decrease in water adsorption for samples 2-B and 3-B could then very well be caused by the extra space occupied by the extra amine chain. The relative areas seem to fit this picture very nicely in a qualitative way.

The increase in area from the unextracted to the extracted samples can be explained by considering the effect of the physically adsorbed excess amine that extraction removes. Every site covered by a physically adsorbed amine molecule will obviously not be available

to a water molecule. This is substantiated by the fact that the difference is most noticeable in sample 1, from which the greatest amount of material was extracted.

From an examination of the areas calculated from the methanol isotherms, such a clear cut explanation does not seem possible. The apparent odd relative values are perhaps due to the fact that not only physical adsorption of the van der Waals type is operative, but that also there is some direct association between the methanol molecule and the amine chains, such as a slight solvation effect. This would also explain the much greater uptake of methanol over water.

Isosteric Heats of Adsorption and Heats of Immersion

From Figures 8 and 9, it is seen that the heat effects associated with the adsorption of water and methanol on the three extracted samples are quite low, being in the range of the heat of liquifaction of the adsorbate. This is strong evidence of the physical van der Waals type of adsorption. The curves also tend to approach this heat of liquifaction as the amount adsorbed increases. All of the curves but one are of the expected type, with an initially high heat sharply falling off and leveling out. This initially high heat is due to the first adsorbate molecules attaching

themselves to the most active adsorption sites.

Some dissention is seen in the literature regarding the validity of using the Clausius-Clapeyron equation for calculating heats of adsorption for systems that do not exhibit thermodynamic reversibility, demonstrated by the presence of a hysteresis loop in the adsorption-desorption isotherms. The error involved would probably be small, and the method is generally considered to yield a good approximation to the correct values and is quite adequate for qualitative comparison.

From Table 2, it can be seen that the values for the heats of immersion follow very well the relative positions of the isosteric heats of adsorption plots. The values are quite small and the error involved in the measurements is probably large. The negative values obtained with samples 2-B and 3-B in methanol correspond nicely to the pronounced dip of the isosteric heat plots below the heat of liquifaction of methanol. The curve dipping lowest, sample 2-B, shows the greatest negative value. This correlation demonstrates that if the overall area under the isosteric heat plot is negative when compared to the heat of liquifaction of the adsorbent, the overall heat effect due just to the adsorption process is negative, and a negative heat of immersion would be expected.

Suggestions for Further Studies

There is yet a large amount of work that could be done to further the understanding of organic clay complexes. Several projects, suggested by this investigation, are listed below.

1. The inclusion of x-ray diffraction measurements corresponding to each step in an adsorption isotherm. This would perhaps show if inter-penetration of the lamina is taking place to a large enough extent to swell the complex.

2. Heats of immersion determinations on samples corresponding to each step in an adsorption isotherm. This would enable a better correlation between these heats of immersion and the calculated isosteric heats of adsorption.

3. A comprehensive study of a series of complexes, starting with an inorganic clay, followed by complexes formed with successively longer organic amine groups. This would show how the properties and characteristics of these complexes vary with the chain length.

4. Extending the number and types of adsorbates to include a wide variety of polar and non-polar, and organic and inorganic substances. This would supply

more information regarding the basic properties of these unusual substances.

SUMMARY

The clay mineral concept has aided greatly the recent investigations of the properties and structures of clays. The laminar structure of the montmorillonite type clay mineral consists of three basic layers, two silicon tetrahedral layers separated by an aluminum octahedral layer. Isomorphic substitution is responsible for the high cation-exchange capacity exhibited by these materials.

Organic complexes of these montmorillonite clays are basically of two types, adsorption complexes and cation-exchange complexes. The cation-exchange type has received the most attention and investigation. Applications for these complexes are many and varied.

Three organic amine type exchange complexes were studied in this investigation. They were a coconut fatty amine bentonite, a dimethyl dioctadecyl ammonium bentonite, and a dimethyl dioctadecyl ammonium hectorite. Adsorption isotherms of water vapor and methanol vapor at 20°C and 37°C, and of nitrogen at -194.7°C were determined on a gravimetric type adsorption balance. B.E.T. plots were determined and effective surface areas calculated. These areas ranged from 30.3 to 44.6 square meters per gram for water adsorption and from 59.1 to

77.1 square meters per gram for methanol adsorption. Areas calculated from the nitrogen isotherms were much smaller, and it was assumed that these corresponded to the external area of the clay crystallites.

Isosteric heats of adsorption were calculated from the Clausius-Clapeyron equation with data from the isotherms at the two different temperatures. These values were plotted versus amount of material adsorbed. Heats of immersion of evacuated clay complex samples were determined calorimetrically in both methanol and water. These were correlated roughly with the isosteric heats of adsorption plots.

Suggestions for further work in the study of these compounds were made, including the extension of number and type of adsorbents and adsorbates.

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