# AN ABSTRACT OF THE THESIS OF

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Title   WATER AND METHANOL ADSORPTION ON A SERIES OF

ORGANIC COMPLEXES OF MONTMORILLONITE

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Water and methanol adsorption isotherms at 25° and 37° C. were determined on a series of organo-bentonite clays. The clays differed in the length of the carbon chain attached to the amine adsorbed in the cation exchange position. The amines used had carbon chains of 4, 6, 8, 10, 12, 14, 16, and 18 carbon atoms. Nitrogen isotherms at -195.8 were also determined. The apparatus used was a gravemetric adsorption balance using quartz springs with a sensitivity of about one millimeter extension per milligram of load.

The isotherms were typical type II isotherms and gave good B. E. T. plots. Effective surface areas were calculated from the B.E. T. plots. Isosteric heats of adsorption were calculated using the Clausius-Claperon equation, with data from the isotherms at the two temperatures.

WATER AND METHANOL ADSORPTION ON A
SERIES OF ORGANIC COMPLEXES
OF MONTMORILLONITE

by

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# ACKNOWLEDGMENT

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# WATER AND METHANOL ADSORPTION ON A
## SERIES OF ORGANIC COMPLEXES
## OF MONTMORILLONITE

## INTRODUCTION

The term clay has no genetic significance, but traditionally

implies an earthy, fine grained material which becomes plastic when

mixed with a small amount of water. Clays are usually formed by

weathering, hydrothermal action, or deposition as sediment.

Due to their uses in ceramics and agriculture, the study of

clays goes back many years. Early investigators found clays had

many varying properties, and even clays that appeared to be the

same had very different properties.

Prior to 1920 there was no logical order to the development of

clay theories. Of the variety of theories held at this time, several

had wide following.

One of the oldest theories was that all clays are composed of

a single pure clay substance called Kaolinite. Differences in clays

were ascribed to the presence of impurities. Since the clays of im-

portance in ceramics and agriculture are composed almost wholly

of Kaolinite this theory persists in some areas. It has now been

established that there are some clays that contain no Kaolinite at all.

Another widely held concept was that the essence of all clays

was a colloidal complex, which was thought to be amorphous as were

all colloids. This complex was thought to be organic or inorganic

depending upon the particular clay. Van Bemmelin (53) and Stremme

(51) regarded the complex not as a definite compound, but rather as

a loose mixture of the oxides of silicon, aluminum, and iron. Later

Thugut (52), Bradfield (2) and others showed clays did not contain

any colloidal oxides. Van Bremmelen (53), and later Stremme (51),

found two "colloidal" fractions, one soluble in hydrochloric acid

and one insoluble in hydrochloric acid but soluble in concentrated

sulfuric acid. Mellor (35) and Searle (46) also developed the idea

that there were two essential components of clay.

Wiegner (54) saw the clay as made up of three parts: 1) a ker-

nel 2) a layer of adsorbed anions in contact with the kernel 3) ex-

changeable cations. The kernel was considered to be a hydrous

compound, chiefly of alumina and silica of variable composition

and of unknown structure.

Another slight variation that has been carried to the present

in the work of Mattson (32) is that the colloid complex is made up

of a relatively inert framework of silica, iron and aluminous mater-

ials encased in an amorphous envelope of silica, alumina, iron,

alkaline earths, and alkalies of varying percentages. In light of

X-ray evidence of the crystalline nature of clays, Mattson (31) has

modified his theory by postulating a crystalline kernel covered by

an amorphous coating.

It is generally recognized that the small size, usually under 2 microns, of clay particles is one of the reasons for their special properties. Oden (38) suggested that size is the major factor and clays can be composed of almost any minerals.

## Clay Mineral Concept

For many years students of clay materials have suggested that clays are composed of extremely small particles. Among the earliest that held this theory were Le Chatelier (28) in 1887 and Lowenstein (29) in 1909. There were no adequate tools prior to 1920 or 1925 to prove this theory, so the theory is not new, but has only recently been well established.

In 1923 and 1924 Hadding (14) in Sweden and Rinne (41) in Germany independently published X-ray diffraction analysis of clay materials showing crystalline material in even the finest clay fractions and that the clay particles were composed of a limited number of minerals, called clay minerals. Ross (45) and colleagues later added X-ray analysis which substantiated their findings.

By 1930 the clay mineral concept was firmly established. Today it is accepted by most students of clays. There were a few exceptions, notably Mattson, who held to the idea that the essential part of clay was an amorphous material that is not shown by X-ray analysis.

According to the clay mineral concept, clays are composed of extremely fine crystalline particles of one or more members of the clay minerals. The clay minerals are essentially hydrous aluminum silicates with magnesium or iron proxying wholly or in part for the aluminum. Some clays are composed of only one clay mineral, but many are composed of several members of the clay mineral group. In addition to clay minerals some clay materials contain varying amounts of non-clay materials.

Investigations into the structure of layer silicates by Pauling (39) provided basic ideas permitting the elaboration and elucidation of many clay materials.

## Structure of Bentonites

Most clay minerals are composed of two main structural units. One such unit consists of a silicon atom surrounded by four oxygen atoms or hydroxyl groups. As predicted by electrostatic theory, the oxygens surround the silicon in a tetrahedral structure, with the four oxygen atoms equidistant from the silicon atom. These silicon tetrahedra can condense and form one, two, or three dimensional structures. Each unit, no matter how complex, contains the primary silicon tetrahedra. The structure that is most important in clays is the layer or sheet structure containing the $(Si_2O_5)^=$ unit (Figure 1).

The other structural unit important in clays is the alumina

| | | |
|---|---|---|
| 1 | O | -2 |
| 1 | Si | +4 |
| 3 | O | -6 |

**TETRAHEDRAL ORTHOSILICATE UNIT $(SiO_4)^{-4}$**

| | | |
|---|---|---|
| 2 | O | -4 |
| 2 | Si | +8 |
| 1 + 1/2 (4) | O | -6 |

**SHEET OR LAYER SILICATE UNITS $(Si_2O_5)^{\pm}$**

| | | |
|---|---|---|
| 3 | OH - | -3 |
| 1 | Al | +3 |
| 3 | OH | -3 |

**ALUMINUM OCTAHEDRON $Al(OH)_6^{-3}$**

| | | |
|---|---|---|
| 6 | OH | -6 |
| 4 | Al | +12 |
| 6 | OH | -6 |

**GIBBSITE $(Al(OH)_3)_n$**
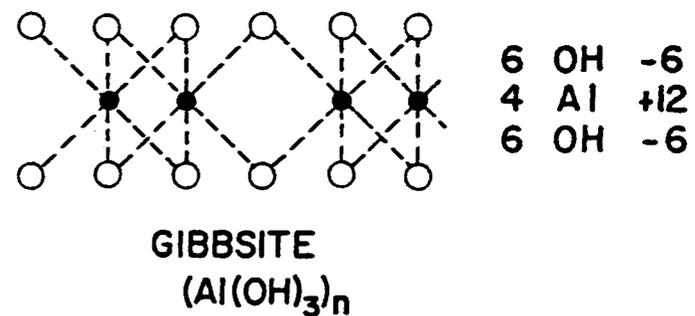
FIGURE I.   THE BUILDING BLOCKS FOR MONTMORILLONITE TYPE CLAYS.
ALL ATOMS HAVE BEEN PROJECTED INTO ONE PLANE.

octrahedra. The arrangement of six groups around the aluminum

atom takes the form of an octrahedron (Figure 1). The aluminum

unit important in clays is that of aluminum hydroxide $(Al(OH)_3$ in

the form of gibbsite. Gibbsite is a laminar type crystal that can

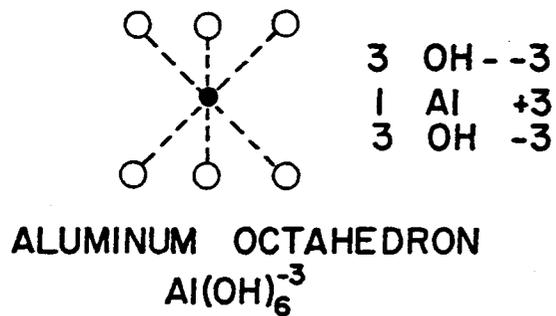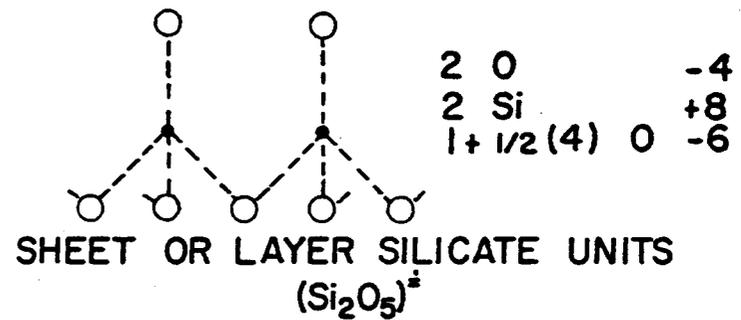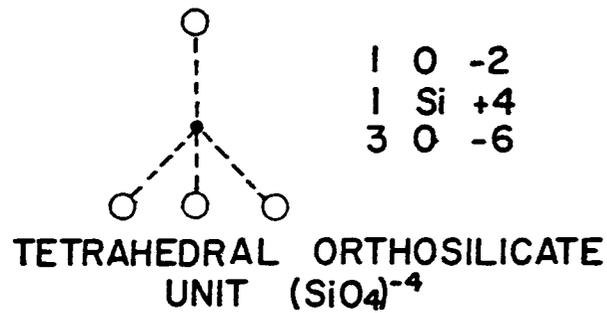extend itself continuously in two dimensions.

In the $(Si_2O_5)^=$ silicate unit there are unattached bonds that

lie in a direction normal to the plane of the crystal. If these bonds

are condensed with the gibbsite layer through its hydroxyl bonds we

have a combined crystal of silicate and gibbsite layers. If further

condensation takes place on the other side of the gibbsite crystal

we form a bond of the type Si-O-Al-O-Si. This leads to the struc-

ture of pyrophyllite (Figure 2) as proposed by Pauling (39). This is

a laminar structure extending continuously in two dimensions and

presenting planar surfaces that are populated with oxygen atoms.

This oxygen populated face presents an active adsorption surface

and is largely responsible for adsorption type complexes.

Pyrophyllite can be considered as the parent compound of the

montmorillonite group. In the montmorillonites variations arise due

to isomorphic substitutions in the crystal lattice. These slight vari-

ations lead to considerable differences in the properties of these

clays. No isomorphic substitution is believed to occur in pyrophyl-

lite itself, consequently it contains no calcium or magnesium and

little or no exchangeable cations. Water and other polar liquids do
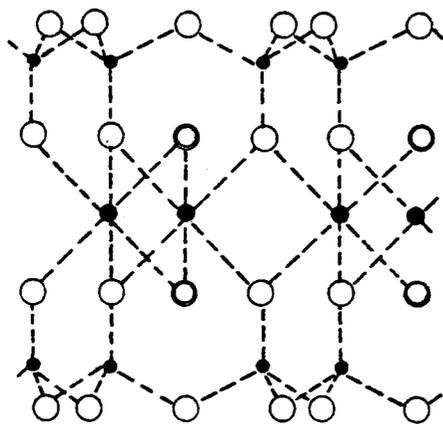
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 6 | O |   |   |   | -12 |
| 4 | Si |   |   |   | +16 |
| 4 | O | + | 2 | OH | -10 |
| 4 | Al |   |   |   | +12 |
| 4 | O | + | 2 | OH | -10 |
| 4 | Si |   |   |   | +16 |
| 6 | O |   |   |   | -12 |

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

not easily wet the surface of silicate lamina and so the clay does

not swell or expand in these media.

The isomorphic substitutions within the montmorillonite group

consist mainly of $Mg^{2+}$ replacing $Al^{3+}$ in the octahedral positions

and $Al^{3+}$ replacing $Si^{4+}$ in the tetrahedral positions.

In Bentonite $Mg^{2+}$ replaces some of the $Al^{3+}$ in the octrahedral

positions. The formula suggested by Ross and Hendricks (43) for

Bentonite is $(Al_{1.56}Mg_{.33})Si_4O_{10}(OH)_2 \cdot Na_{.33}$

There is some contention regarding the structure of Bentonite,

but the structure originally proposed by Hoffman, Endel, and Wilm

(21) has been widely accepted and is in accord with the structure of

pyrophylite presented by Pauling.

## Cation Exchange Capacity

As can be seen from Figure 2 pyrophylite has no electrostatic

charge on the unit cell. When there is isomorphic substitution of one

ion for another in the clay lattice the resulting change must be neu-

tralized by ions outside the lattice for the charge to remain zero on

the unit cell. Thus when $Mg^{2+}$ is substituted for $Al^{3+}$ there must

be an ion of 1+ charge outside the lattice to correct this charge un-

balance. These cations are located on the exterior surfaces of the

laminar sheets and are held by electrostatic attraction. The exter-

nal cation is easily hydrated in aqueous media and since it occupies

no fixed position in the structure it is easily replaced by other cations. This property is known as cation exchange, and varies greatly among clays. The cation exchange capacity for the montmorillonite group varies from 80 to 150 milliequivalents per 100 grams of clay.

These exchangeable cations, as well as giving the clay a cation exchange capacity, also produce differences in the characteristics of the clays. The strong hydrophilic nature of most of the cations is due mainly to the ease with which they pick up water of hydration. Much work has been done on these hydration reactions as a function of the cation present. Hendricks, Nelson, and Alexander (19) studied water adsorption by montmorillonites as a function of the cation present in the exchange position.

Hendricks and Jefferson (18) found the water of hydration of montmorillonites existed as layers of joined hexagonal nets. The swelling properties arise when layers of this interlaminar water build up, pushing the layers apart.

To a small extent clays exhibit exchanges of anions. These exchanges usually arise at the edges of the laminar crystal, where chloride, fluoride, and phosphate ions exchange with the hydroxyl groups in the lattice. This type of exchange has not received much attention and the present state of understanding is not well advanced.

# HISTORY OF ORGANIC COMPLEXES OF CLAYS

Organic complexes of clays are usually divided into two classes, adsorption complexes and cation exchange complexes.

Adsorption complexes are considered to be those in which physical adsorption of organic groups takes place on the oxygen populated surfaces of the clays. Cation exchange complexes are those in which an inorganic ion in a cation exchange site is replaced by an organic group, usually an amine. There are some groups that fall in neither category, however.

Emerson (7) studied organo-clay complexes of bentonite and high polymers and found that only the edge faces of the crystal were involved. He suggests that in these "peripheral" complexes the polymer links the edge faces of the clay crystal by hydrogen bonding to the oxygen and hydroxyl groups. Decul (6) prepared phenyl derivatives of bentone clays and found the mode of attachment was neither physical nor cation exchange, but direct chemical reaction with the clay lattice.

## Adsorption Complexes

Since many of the nonionic and organic molecules have dipole moments and the surfaces of the clay crystals are also polar, one would expect association between the clays and polar molecules.
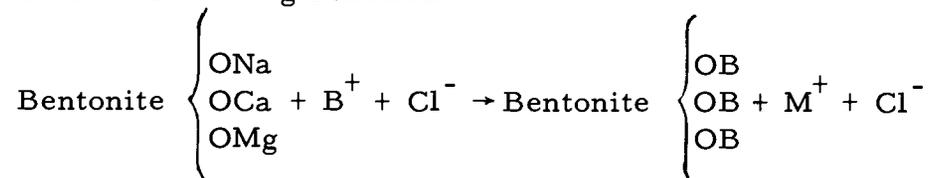
Bradley (3) found that many organic molecules displace the inter-laminar water, but not the ions in the cation exchange positions. From X-ray diffraction data he postulates that the organic polar molecule is held to the clay surface by C-H--O type hydrogen bonds between methylene groups and the oxygen populated surface of the clays. Bradley's work has been supported by Mac Ewan (30). A series by Green-Kelly (10, 11, 12) with pyridine and saturated organic rings and chains showed two orientations of the molecules, one where the plane of the ring is parallel to the silicate sheet, and the other where the ring is perpendicular to the silicate layer. This latter orientation occurs only at high concentrations.

## Cation Exchange Complexes

Due to the large cation exchange capacities of the bentonite clays, much work has been done involving organic ions in the exchange position. Many of the common organic cations contain amine groups and most of the work has been in this area. Some study has been done with other organic groups, such as the methylated complexes reported by Berger (1).

Smith (50) was the first to use a systematic approach to the study of cation exchange with organic groups. He found that the reaction was in stoichiometric ratios and that the clay becomes more hydrophobic as the size of the organic group increases. He

postulated the following reaction:

$$\text{Bentonite} \begin{cases} \text{ONa} \\ \text{OCa} \\ \text{OMg} \end{cases} + B^+ + Cl^- \rightarrow \text{Bentonite} \begin{cases} \text{OB} \\ \text{OB} \\ \text{OB} \end{cases} + M^+ + Cl^-$$

Gieseking (9) found that the organic amines increased the 001 spacing

when adsorbed in the exchange position, and that the organic amines

were replaced easily by other organic amines, but not by hydrogen

ions. Hendricks (17) discovered that the cation exchange capacity

involving organic groups is the same as that for the inorganic cat-

ions. Extremely large cations of over $80\mathring{A}^2$ in effective area do not

completely neutralize the clay, due to overlapping of exchange sites.

This condition is not observed with the smaller groups, and is con-

sidered to be due to not only coulombic forces between ions, but also

to van der Waals forces between the clay and the organic ion. Jor-

dan (24) plotted 001 spacings from X-ray data versus carbon chain

length and found an increase of $4\mathring{A}$ in separation. The van der Waals

radius of the methyl radical is about $4\mathring{A}$ so this indicates that the

carbon chain lies parallel to the silicate layer.

Slabaugh (47) in 1954 and Cowen and White (5) in 1958 studied

the energies involved in the cation exchange reaction with organic

amines. Slabaugh calculated equilibrium constants for the reaction:

$$\text{Na-Bentonite} + RNH_3^+ \rightarrow Na^+ + RNH_3\text{-Bentonite}$$
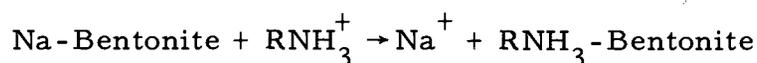
He found that the equilibrium constant increased with the length of

the carbon chain.

When an amine ion exchanges with an inorganic ion in the cation exchange position of the clay, the hydrophilic surfaces are transformed into hydrophobic surfaces (47). The surface as well as being hydrophobic is also very organophilic. This phenomena has been studied by Slabaugh and Kennedy (48), Green-Kelly (13) and Jordan (22). It has been observed that the organophilic properties of the clays are negligible until a carbon chain length of ten or 12 atoms is reached (24).

Barrer et al. in a series of papers since 1955 have made studies of the interlaminar sorption by montmorillonite. Barrer has, in effect, held the platelets apart by intercallation of substituted amines between the crystal lamina. This opens up areas of the clay to a wide number of organic compounds and leads to selective adsorption. This suggests the use of this type of clay as an ion exchange resin.

# THEORY

## Types of Adsorption

Adsorption can be described as the process by which atoms or molecules of one material interact with the surface or interface of another material. This interaction takes place in two ways, called chemical adsorption, or chemisorption, and physical adsorption. In chemisorption the adsorbate chemically bonds to the adsorbant in an irreversible, or at best difficulty reversible, reaction. The energy involved is about the same as that for the formation of a chemical bond, or about 50 to 100 kilocalories.

In the second and most common type of adsorption, physical adsorption, the reaction is reversible and the energies involved are near the heat of condensation for the adsorbent. Physical adsorption can almost be considered as a process of condensation of a gas on the solid surface. Since the primary forces involved in condensation are van der Waals forces, this is sometimes called van der Waals adsorption. The most general method of distinguishing between chemisorption and physical adsorption is through the energies involved, although a clear cut decision is not always possible.

## Theories of Adsorption

Since one of the most characteristic properties of the surface of a solid is its ability to adsorb gases and vapors, much work has gone into the theory of adsorption. One of the first equations for adsorption is credited to Freundlick, since it was first used in several of his early papers.

In 1915 Langmuir (27) proposed an equation based on the assumption that adsorption occurred as a monomolecular film. He proposed a "dynamic equilibrium" such that at equilibrium the rate of adsorption equaled the rate of desorption. While Langmuir's equation fits experimental data only in a limited number of cases, it is still valuable as a basis for further development of adsorption theory.

In 1938 Brunauer, Emmett, and Teller (4) extended the Langmuir isotherm to include multilayer adsorption. The theory retains the concept of fixed adsorption sites, but allows for the formation of an adsorbed layer more than one molecule thick. The state of "dynamic equilibrium" proposed by Langmuir is assumed to exist at the formation of each successive molecular layer. This theory gives a simple procedure for determining the monolayer capacity, and therefore the surface area of the solid. The major assumption of the B. E. T. theory is that the forces responsible for condensation

are also responsible for multimolecular adsorption.

Derivation of the B. E. T. equation for a monolayer, results

in the following equation:

$$P/(P_o - P)W_m = 1/W_m C + C - 1/W_m C \cdot P/P_o$$

where P is the pressure of the gas, $P_o$ is the saturation pressure

of the gas, W is the weight of the gas adsorbed per unit weight of

adsorbent, $W_m$ is the weight of gas adsorbed at the monolayer, and

C is a constant related to the heat of adsorption.

If $P/(P_o - P)W$ is plotted versus $P/P_o$, a straight line is ob-

tained between $P/P_o$ of 0.01 and 0.35 having a slope of $C - 1/W_m C$

and an intercept of $1/W_m C$. Solving for $W_m$ we find $W_m = 1/slope$

+ intercept). The surface area can now be found if the molecular

area of the adsorbate molecule is known.

Another method for calculation of surface areas is the Harkins-

Jura method (17). Harkins and Jura point out that for a condensed

film on a solid the film pressure $\pi$ and area $\sigma$ relationship is given

by the equation:

$$\pi = b - a\sigma$$

The equation is usually used in the following form:

$$\text{Log } P/P_o = B - A/V^2$$

where A and B are constants and P and V can be measured experimentally. In this method there is no need to assume a molecular area for the adsorbate.

The Harkins-Jura and the B. E. T. methods give very good agreement considering that the B. E. T. theory is based on kinetics and the Harkins-Jura theory is based on thermodynamics.

A new method that is useful for determining areas of a series of like solids, is a combination of theories by Frenkel (8), Halsey (15), and Hill (20). Measurements of marine sediments by Slabaugh and Stump (49) using the Frenkel, Halsey, Hill equation agree closely with areas determined by the conventional B. E. T. method.

## Hysteresis

In theory the adsorption, desorption curves should fall on the same curve, but in practice this is not always found to be true. The resulting phenomena is termed hysteresis.

There have been many attempts to explain hysteresis, but no theory has yet explained all cases of hysteresis. It is probably safe to say that hysteresis is caused by several mechanisms, each of which may be applicable to a particular system. The usual explanation is capillary condensation. Adsorption on small capillaries takes place by the usual multilayer adsorption, but desorption takes place on the meniscus of the small capillaries. The vapor pressure

lowering over a meniscus of small radius is the reason for the hysteresis loop. Pierce and Smith (40) however, claim capillary condensation is not necessary, but explain hysteresis by postulating adsorption in small clumps, over the adsorption sites, that eventually merge forming larger clumps. Desorption then takes place on these larger clumps.

Another explanation for hysteresis is that structural changes take place in the solid upon adsorption. Hirst (21) proposes a mechanism where the platelets of a laminar solid are pushed apart by the film pressure of the adsorbate, causing swelling. This explanation is particularly applicable in clay systems such as the bentonites.

## Isosteric Heats of Adsorption

The adsorption of a gas on a solid surface usually takes place with the evolution of heat. In physical adsorption this evolution of heat is rather small, on the order of the heat of condensation. This isosteric heat can be determined in two different ways. It can be measured directly in a calorimeter, or it can be calculated from adsorption isotherms at different temperatures.

The value of the isosteric heat can be determined at any constant relative surface concentration $W/W_m$ graphically by using the Clausius-Claperon relationship:

$$(dlnP/dt)_\theta = q_{st}/RT^2$$

By plotting $\ln P$ vs $1/T$ a slope of $-q_{st}/R$ at any constant $W/W_m$ is obtained. The main disadvantage to this method is that it is necessary to have adsorption isotherms at several different temperatures. The most common practice is applied to isotherms at two different temperatures and using the integrated form of the Clausius-Claperon equation:

$$\ln P_2/P_1 = q_{st}/R \cdot T_1 T_2/(T_2 - T_1)$$

Theoretically this relationship is valid only for reversible systems, but it is commonly used for systems exhibiting moderate hysteresis. The assumption that the equation is valid for these systems should involve no great error in $q_{st}$, but values thus determined should be only used qualitatively and with discretion.

# 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 (34) (Figure 3). The main manifold in a vacuum system has two chambers for adding and storing the adsorbate, one for liquids and one for gases. Also attached to the main manifold are a mercury and an oil manometer, a McLeod gauge, and a secondary manifold. Each sample is held in a bucket made from 0. 0005 inch tin foil fitted with a handle of 0. 0056 inch copper beryllium wire. Samples plus buckets and extension rods are suspended from quartz springs that have a sensitivity of about one millimeter extension per milligram of load. Between the spring and the sample bucket is a glass fiber with color coded markings. Using an optical system, these markings are projected on a scale on the wall about seven feet away. The springs are calibrated in milligrams per scale division by hanging calibrated weights from the springs and reading the coded markings projected onto the scale. Sensitivity is about 0. 8 milligrams per scale division. The scale can be read to 0. 05 divisions giving about ±0. 04 milligram sensitivity for a 400 milligram sample. The sample, bucket, spring, and extension rod are enclosed
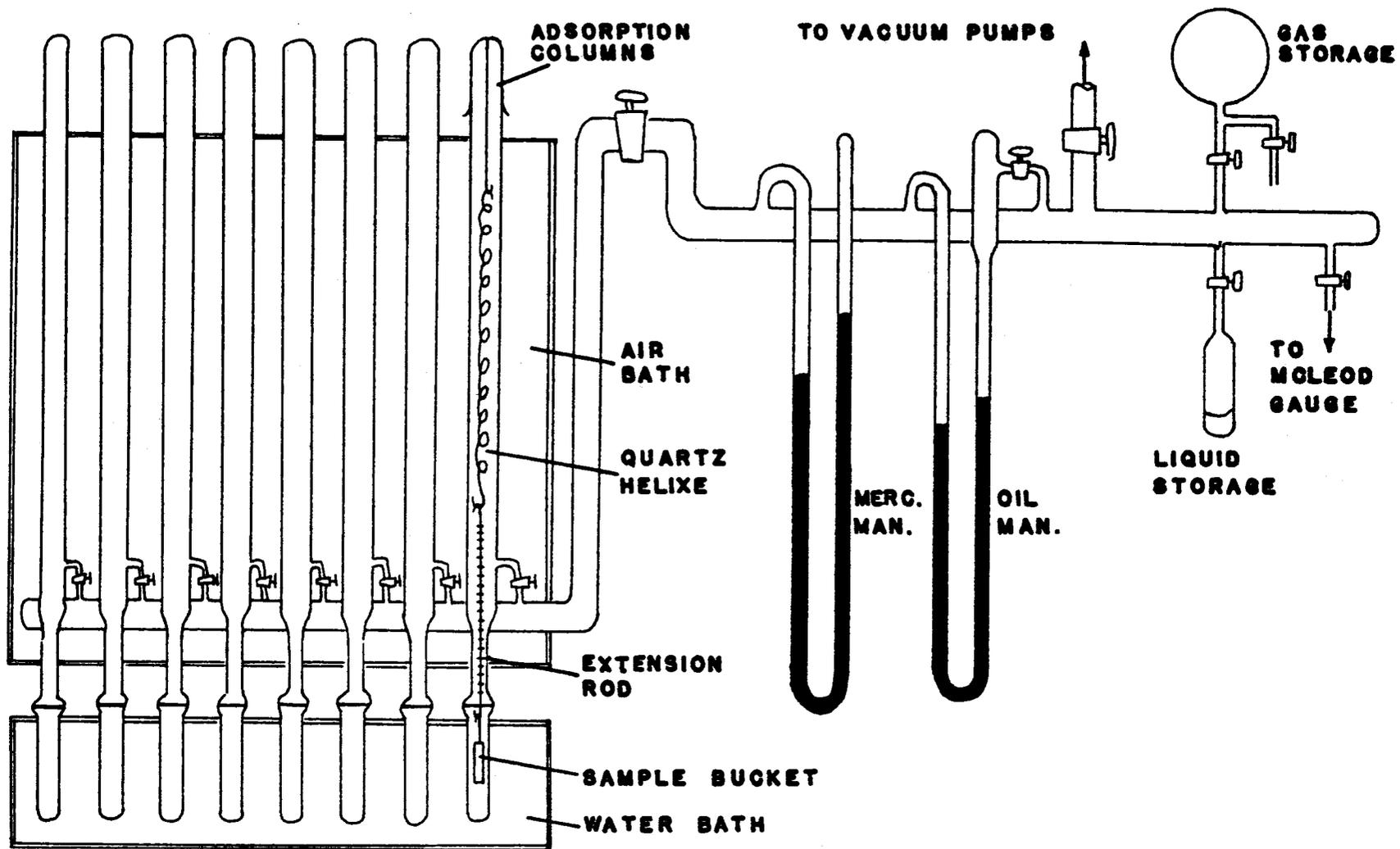
FIGURE 3 GRAVIMETRIC ADSORPTION BALANCE

in a glass sample tube which is connected to the secondary manifold in such a way that the eight tubes can be isolated individually. The upper end of the sample tubes are enclosed in a constant temperature air bath at 28 ± 0.5 degrees centigrade. Sample temperature is controlled by immersing the lower end of the sample tube in a constant temperature water bath that was accurate within ±0.1 degrees. For liquid nitrogen runs the water bath was replaced with dewar flasks containing liquid nitrogen.

## Preparation of Samples

The adsorbents used in this investigation were a series of organic amine substituted bentonites. The original clay was a Wyoming bentonite supplied by Baroid Division of the National Lead Company. The amines used were as follows:

    Sample 4C four carbon chain
    Sample 6C six carbon chain
    Sample 8C eight carbon chain
    Sample 10C ten carbon chain
    Sample 12C twelve carbon chain
    Sample 14C fourteen carbon chain
    Sample 16C sixteen carbon chain
    Sample 18C eighteen carbon chain

The clays were prepared by dispersing one percent by weight of clay in water. The amines were dissolved in isopropyl alcohol and titrated with acetic acid to form the amine acetate. The amine acetate is added to the clay solution in about 25% excess assuming a

cation exchange capacity of 100 milliequivalents per 100 grams.
After setting for several hours the clay solution is filtered. The
clay is then extracted in isopropyl alcohol in a soxhlet extractor,
dryed and then ground fine enough to pass through a 170 mesh screen.
Sample weights are weight in air.

## Procedure

Adsorption isotherms were determined for water and methanol
at 25 and 37 degrees centigrade. Nitrogen isotherms at -195.8 were
also run for comparison. Samples were weighed into foil buckets
and then sample, bucket, and extension rod were suspended from the
springs. Sample weight was approximately 300 milligrams and the
foil buckets weighted about 100 milligrams, giving an overall weight
of approximately 400 milligrams. Samples were outgassed at room
temperature for 48 hours. Care was taken when initially evacuat-
ing the samples as trapped gases sometimes cause them to bump
when evacuated too rapidly. After outgassing, a zero reading was
taken, and the adsorbate was let into the system in small increments.
A check on the equilibrium time showed about one hour was required
for the water and methanol and 15 minutes for the nitrogen. There-
fore two hours was allowed between readings for water and methanol
and one-half hour for nitrogen. When equilibrium was reached the
spring extension on the wall chart was read and the pressure

determined. Small pressures were read by projecting the mercury manometer on the wall, approximately 17 feet away and gaining a magnification of 25. Pressures could be read in this manner to ± 0.05 mm. For the next point the process was repeated, with ten or 12 points completing the isotherm.

Desorption runs were made at 25 degrees for both adsorbates, and all runs were checked for reproducibility.

# EXPERIMENTAL RESULTS AND CALCULATIONS

## Adsorption Isotherms and Surface Areas

Water and methanol adsorption on the clay complexes showed typical type II inverted S shaped curves as shown in Figures 4 and 5. Isotherms were found to be reproducible well within experimental error. Adsorption desorption isotherms showed hysteresis at all pressures. B. E. T. plots for water were linear from 0.1 to 0.35 $P/P_o$ as seen from Figures 6 and 7. From the B. E. T. plots values of $W_m$ were obtained, and surface areas were calculated using 10.6 $\overset{\circ}{A}^2$ amd 12.0 $\overset{\circ}{A}^2$ for the cross-sectional area of water and methanol molecules, respectively. Values of $W_m$ and surface areas tabulated in Table 1 are average values for all runs at 25 degrees.

Nitrogen areas were 22.25, 18.93, 14.81, and 7.15 meters squared per gram for samples 6C, 8C, 10C, and 12C.

Errors in $W_m$ ranged from 1.1 milligrams or 3.7% for sample 4C to 0.31 milligrams or 1.36% for 8C with water vapor. $W_m$'s for methanol were calculated for only one plot as the data points for all runs fell on the same curve for each type of sample.
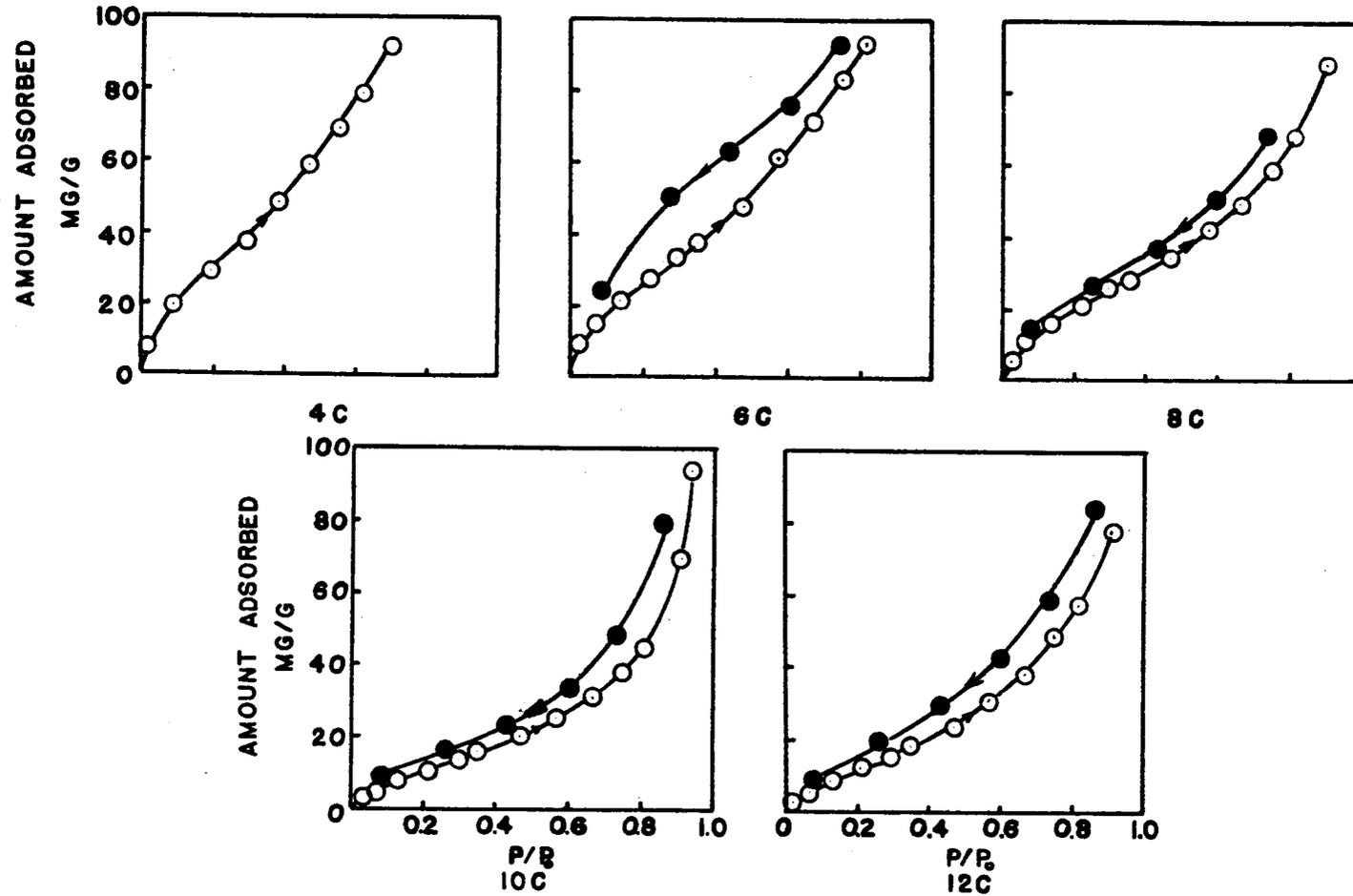
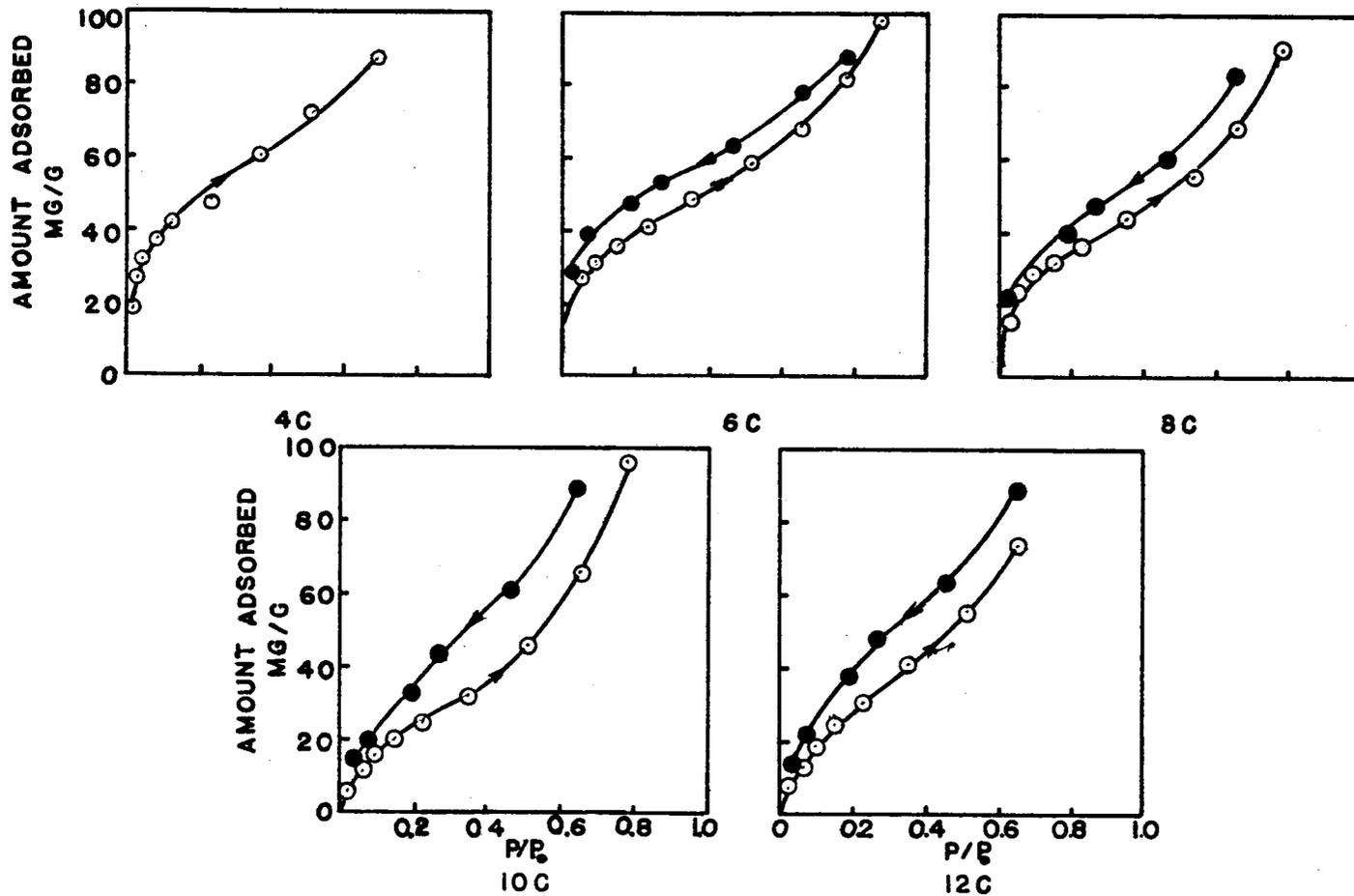FIGURE 4 WATER ISOTHERMS OF ORGANIC CLAY COMPLEXES
AT 25°C

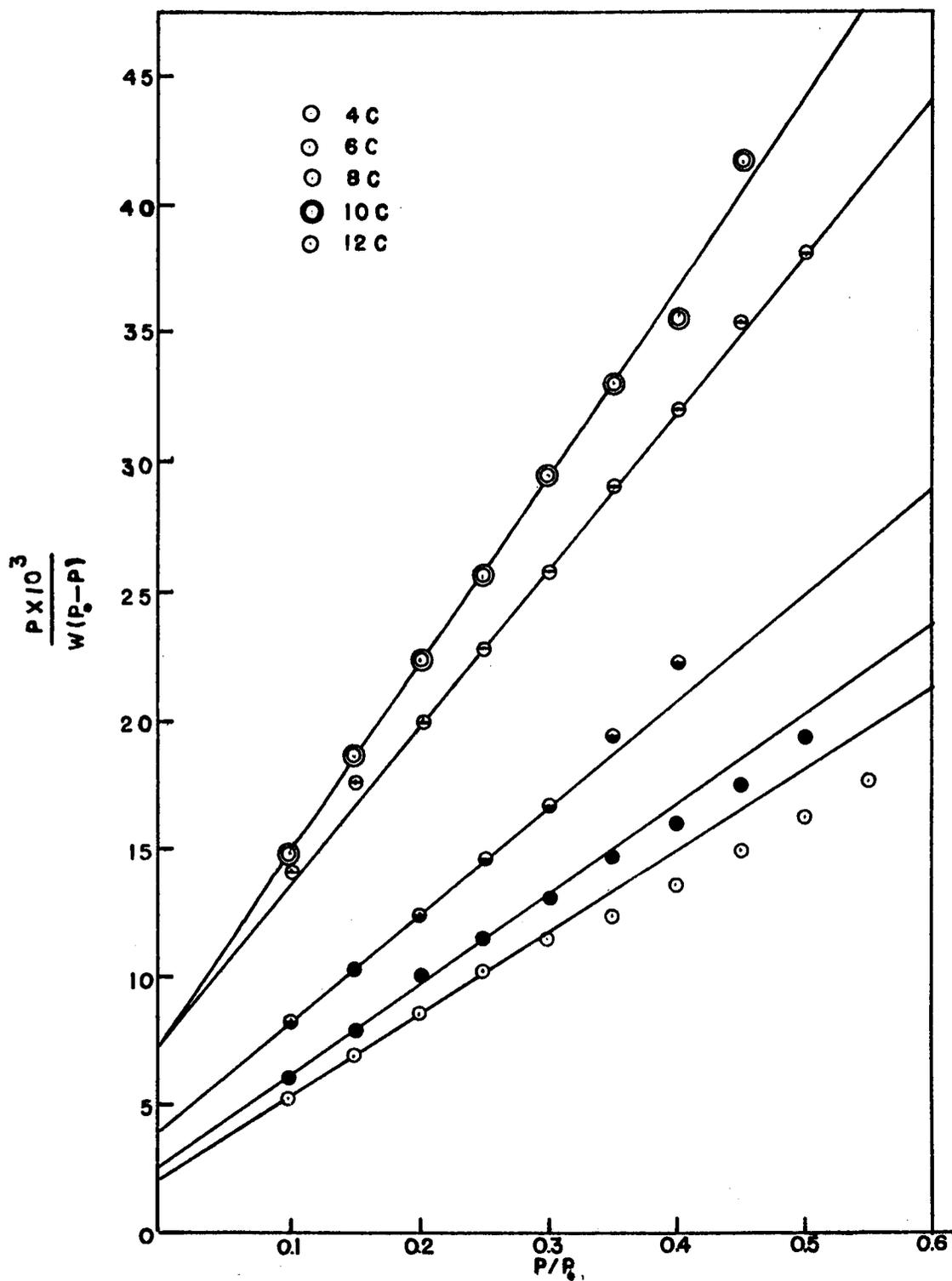FIGURE 5 METHANOL ISOTHERMS OF ORGANIC CLAY COMPLEXES AT 25° C

28

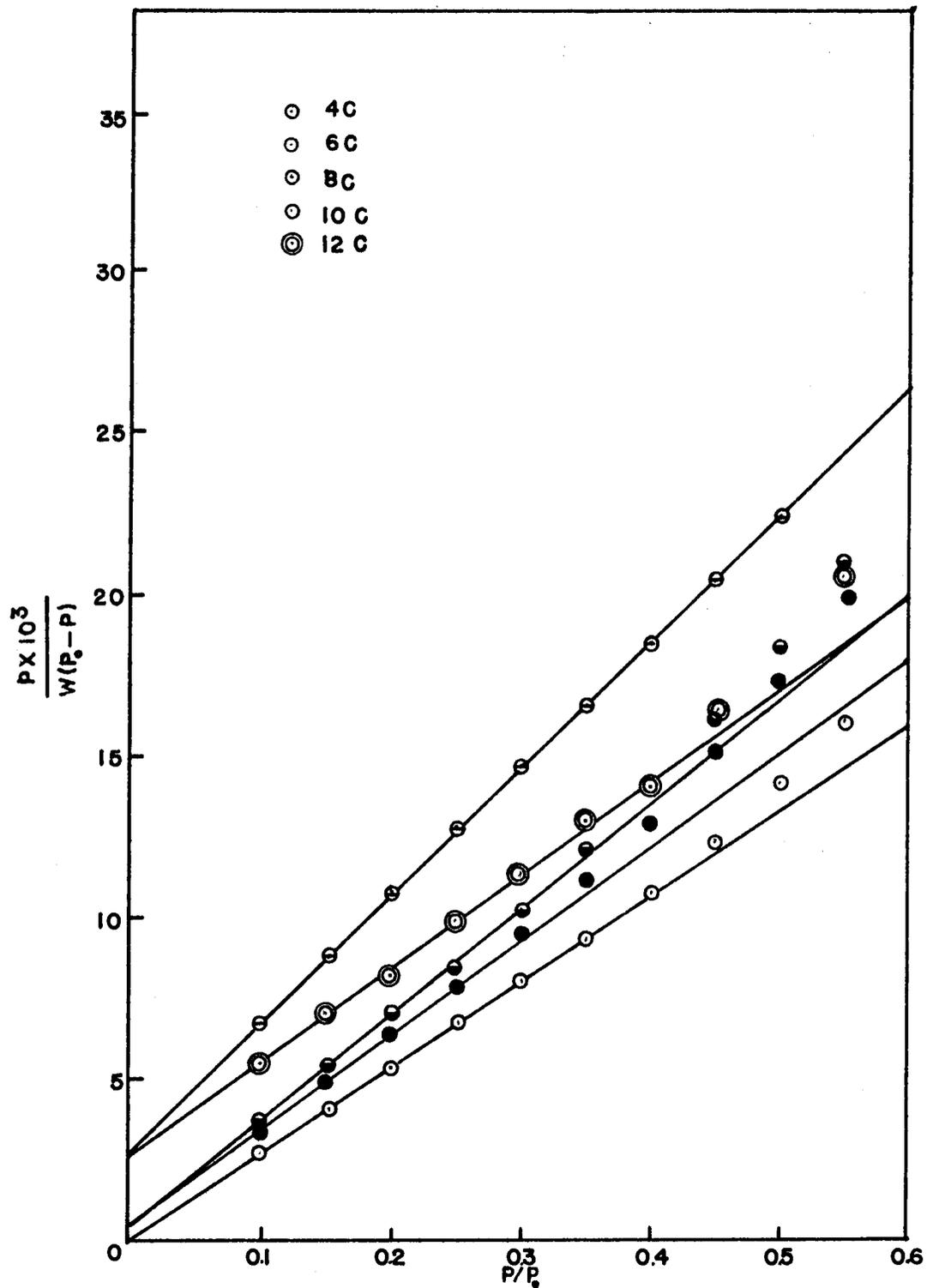

FIGURE 6 BET PLOTS, WATER ON ORGANIC CLAY
COMPLEXES AT 25°C

FIGURE 7  BET PLOTS, METHANOL ON ORGANIC
CLAY COMPLEXES AT 25° C

Table 1. Effective surface areas for organic clay complexes

| Sample | Water | | Methanol | |
|---|---|---|---|---|
| | $W_m$ | Area | $W_m$ | Area |
| | mg/g | $m^2/g$ | mg/g | $m^2/g$ |
| 4 C | 29. 70 | 105. 4 | 38. 17 | 86. 26 |
| 6 C | 25. 51 | 90. 56 | 29. 24 | 66. 08 |
| 8 C | 22. 83 | 81. 10 | 26. 67 | 60. 27 |
| 10 C | 12. 55 | 44. 55 | 23. 15 | 52. 32 |
| 12 C | 15. 00 | 54. 10 | 31. 06 | 70. 19 |
| 14 C | 11. 38 | 40. 40 | 27. 11 | 61. 27 |
| 16 C | 11. 61 | 41. 22 | 27. 11 | 61. 27 |
| 18 C | 10. 73 | 38. 09 | 24. 87 | 56. 21 |

## Isosteric Heats of Adsorption

Adsorption isotherms were run at 37 degrees for both water and methanol. These isotherms showed the same degree of reproducibility as those at 25 degrees. Isosteric heats of adsorption were calculated from the two isotherms using the Clausius-Claperon equation. Isosteric heats for water and methanol on the clay complexes are reported graphically in Figures 8 and 9. Values reported are averages of heats calculated for all runs. Agreement between values was good only after the formation of the monolayer. The heats calculated at low surface coverage showed wide variations between runs,
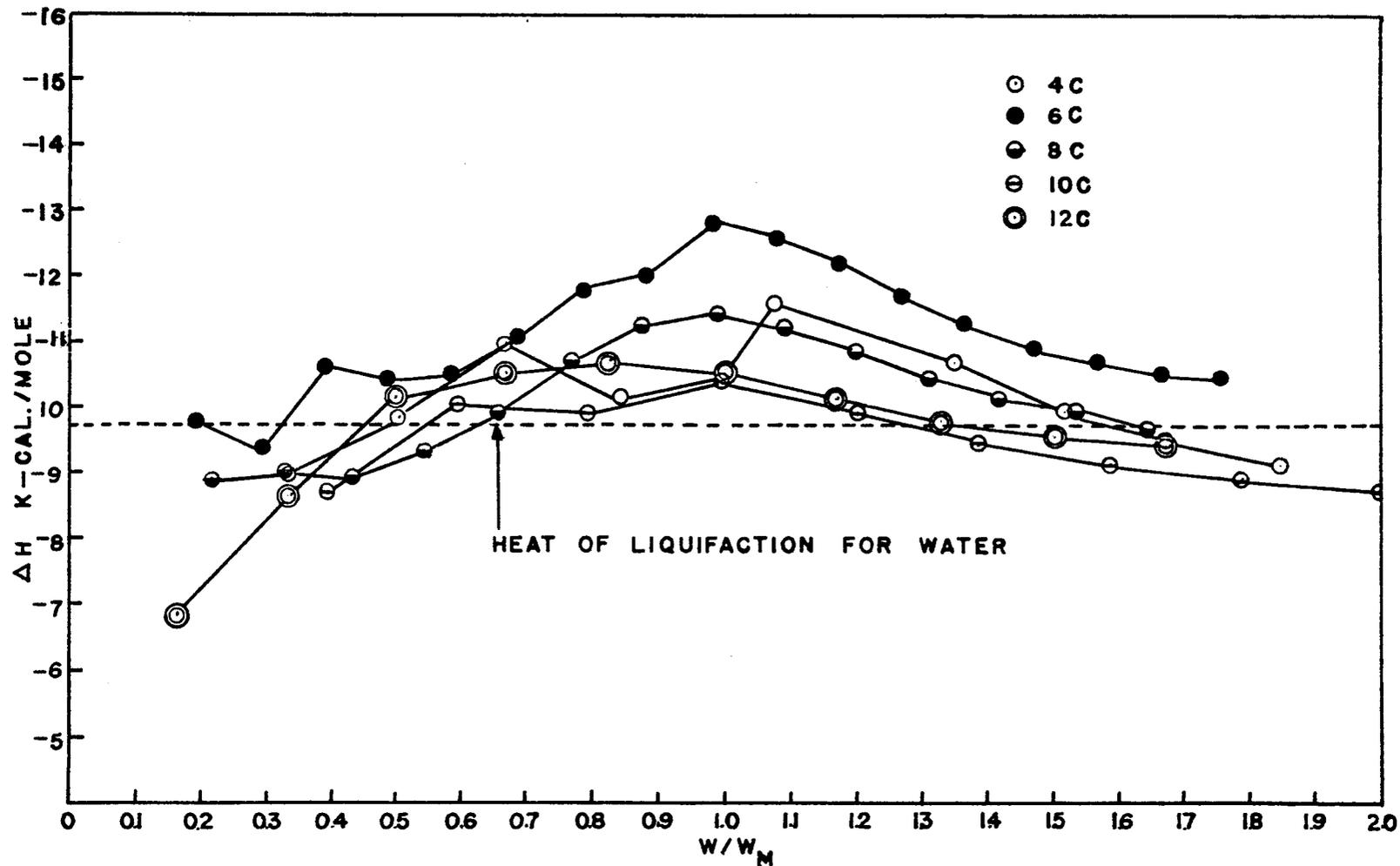
FIGURE 8 ISOSTERIC HEATS OF ADSORPTION OF WATER ON ORGANIC CLAY COMPLEXES
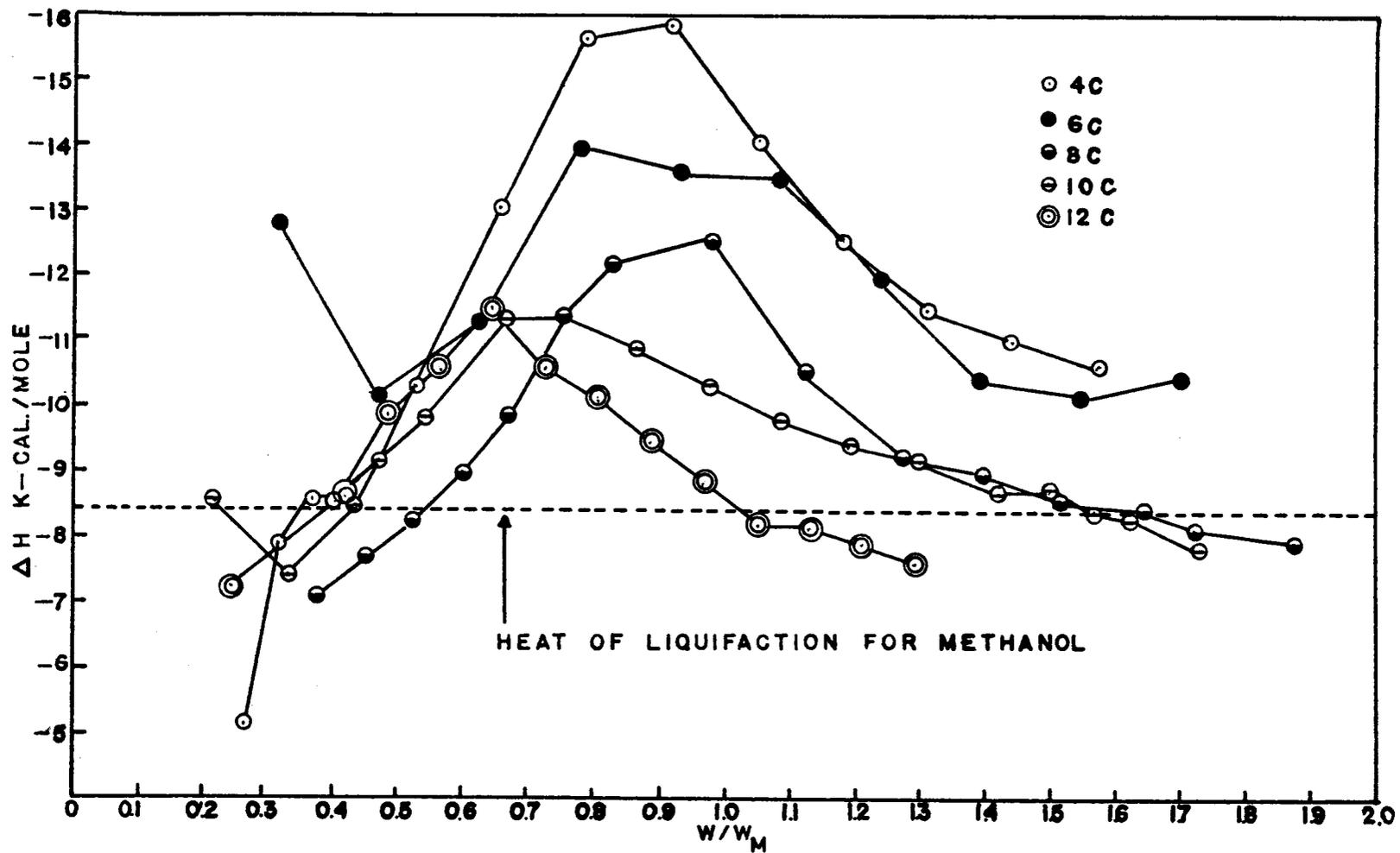
FIGURE 9 ISOSTERIC HEATS OF ADSORPTION OF METHANOL ON
ORGANIC CLAY COMPLEXES

and so values in this region should be viewed only qualitatively.

The heats at low surface coverage were taken from portions of the

isotherms that lie very close together, thus increasing the chances

for error.

Deviation in values of $-\Delta H$ ranged from 8.86% to 1.12%, with

the amount of deviation becoming smaller as values of $W/W_m$ became

larger.

Graphs were not plotted as smooth curves, since data for cal-

culations were taken from selected points on adsorption isotherms.

DISCUSSION

## Effective Surface Areas

The nitrogen areas for these samples are in the range for

clays of this type (37). If these are the external areas of the clays,

then some adsorption between the lamina of the clay must take place

in order to explain the larger areas found with water and methanol.

If the area between the lamina are considered, clays of this type have

a total surface area of about 800 $m^2$/gm, so it can be seen that only

a small amount of the surface between the lamina is being used in the

adsorption.

The carbon chain on the amine in the cation exchange position

lies on the surface of the clay in a zigzag fashion. The packing effi-

ciency for this arrangement is poor and it can be seen that there is

enough surface left uncovered to account for the adsorption of the

water and methanol. As the length of the carbon chain increases,

the amount of surface available for adsorption becomes less and

the effective surface area decreases as seen by the series formed

by samples 4c, 6c, 8c, and 10c. The methanol areas in the region

from 4c to 8c are smaller than the water areas since the surface of

the clay is largely hydrophilic in this region. When the carbon chain

increases to about ten carbons, the surface of the clay starts to

become primarily organophilic, and the methanol areas become larger than the water areas.

At 12 carbons, the X-ray data shows an increase in 001 spacing of about 4Å (24). This indicates that the carbon chains have begun to overlap, forcing the lamina of the clay apart by another 4Å. This increased spacing makes more space available for adsorption and the effective areas to both water and methanol increase. Due to the organophilic nature of the surface the methanol area increases more than the corresponding water area.

Surface areas for 14, 16 and 18 carbon chain amine substituted clays show the same general trend as in the series 4 through 10 carbons for both water and methanol areas. The drop in surface area is less pronounced at the end of the series, than it is at the beginning of the series, but is due to the same mechanism. For the series 12 through 18 carbons the methanol areas are larger than the water areas showing that the surface of the clay is organophilic.

## Isosteric Heats of Adsorption

The isosteric heats for this series of clays show a low heat at low surface coverages, and rise to a maximum near the completion of the monolayer, and then drop to approach the heat of condensation for the adsorbate.

Isosteric heats have been reported that start high and fall

rapidly to approach the heat of condensation of the adsorbate.
Slabaugh and Kennedy (48) reported this behavior for Bentone 18,
34, and 38. Surface heterogeneity is usually given as a reason for
the high isosteric heat at low surface coverage.

The increase in isosteric heats at low surface coverage is
explained by Jurinak and Volman (25) as due to the increasing molec-
ular interaction between adsorbed vapor molecules as the surface of
the adsorbent becomes covered. At the maximum isosteric heat,
multilayer formation is considered to be initiated. As adsorption
continues, the adsorbate assumes liquid-like properties and the
isosteric heat drops to approach the heat of condensation for the
adsorbate. This type of behavior has also been reported by Mooi,
Pierce, and Smith (36).

For the series of clays reported here the isosteric heat ap-
proaches a maximum near the value for the completion of the mono-
layer on all clays for water and all clays except the ten and 12 car-
bon chains for methanol. The maximum isosteric heat for ten and
12 carbons with methanol appears near $W/W_m = 0.65$ to $0.70$. Mul-
tilayer formation before the completion of the monolayer has been
reported before, notably by Jurinak and Volman (25).

SUMMARY

The adsorption of water and methanol vapors on a series of organic complexes of bentonite clays was studied. Adsorption isotherms at 25 and 37 degrees were run and effective surface areas were calculated for runs at 25 degrees. The samples used were Wyoming bentonite that had a series of organic amines in the cation exchange position. The carbon chain attached to the amine group varied in length. Four, 6, 8, 10, 12, 14, 16, and 18 carbon chains were used.

Effective surface areas at 25 degrees ranged from $38.09m^2/g$ to $105.4m^2/g$ for water and from 52.32 to $86.26m^2/g$ for methanol. Nitrogen areas were calculated at -195.8 degrees C and were in the range expected for the external surface area of the clays.

Isosteric heats of adsorption were calculated from isotherms at 25 and 37 degrees C. The isosteric heats showed an increase to a maximum near the value for the completion of the monolayer, then dropped to approach the heat of condensation for the adsorbate.

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