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Ethanol-toluene and methanol-toluene mixtures were employed as binary solutions in studying the solvent selectivity by various homionic bentonites. To measure the small concentration changes due to this adsorption process, a differential refractometer was utilized. Data were obtained in the low alcohol concentration region of the composite isotherms.

The investigation showed that for the ethanol-toluene system the order of decreasing adsorption relative to a given homionic-bentonite was  $\text{Ca}^{2+} > \text{Ba}^{2+} > \text{Na}^+ > \text{NH}_4^+$ , and that for the methanol-toluene system was  $\text{Ca}^{2+} > \text{Ba}^{2+} \sim \text{Na}^+ > \text{NH}_4^+$ . Secondly, it was observed that for a given homionic-bentonite methanol adsorbed to a greater extent than ethanol. From the values for the ionic potential (charge to radius ratio) of the exchangeable cations and the dielectric constant of the alcohols, it was concluded that the dominant mechanism at low concentrations of the alcohol was the solvation of the exchangeable cation by the polar component.

In addition, applicability of the B. E. T. (Brunauer-Emmett-Teller) equation for multilayer vapor-solid adsorption to this system was investigated. The B. E. T. plots were found to be linear in a small concentration range; less than nine percent of the complete isotherm. Moreover, the parameter  $V_m$  was interpreted as being the amount of alcohol required to solvate the exchangeable cation.

Solvent Selectivity by Homionic Bentonites

by

Richard William Vasofsky

A THESIS

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# SOLVENT SELECTIVITY BY HOMIONIC BENTONITES

## INTRODUCTION

### Definition of Clays

According to Grim (24), the term clay refers to a natural, fine grained material, which becomes plastic-like when mixed with a limited amount of water. Clays are essentially composed of silica, alumina, and water, usually with significant amounts of iron, alkalies, and alkaline earths. Particle size appears to be that characteristic which enables one to differentiate between clay and non-clay minerals. In soil science, clay is that grade of material finer than two microns, the reason being that most non-clay minerals concentrate in particles larger than two microns. There are, however, exceptions.

Those clays produced by the alteration of volcanic ash in situ are called bentonites. The dominant clay component of bentonites is montmorillonite, although other clay minerals such as illite and kaolinite may also be present. Cristobalite, a crystalline form of silica, is a non-clay mineral appearing in particles less than one micron in diameter. Being intimately mixed with the mineral montmorillonite, it may account for as much as 30% of the bentonite.

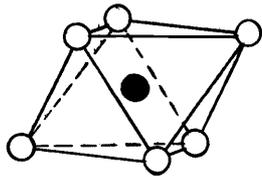
### Structure of Clay Minerals

The following is a brief discussion concerning clay structure.

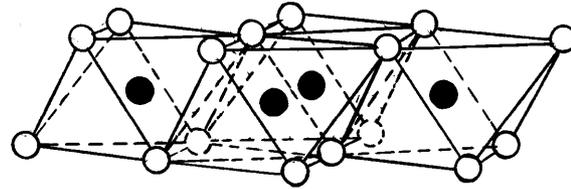
More detailed discussions may be found in textbooks by Grim (24, 25), van Olphen (37), McBain (34), and Brown (14).

In 1930, the basic structure of clay minerals was described correctly by Pauling (35). Clays are composed essentially of two fundamental structures, the octahedral sheet and tetrahedral sheet. As shown in Figure 1a the octahedral unit consists of a metal center, aluminum, magnesium, or iron, etc., octahedrally coordinated to six oxygen or hydroxyl groups. These individual units, by sharing a face of the octahedron, are bonded together so as to form sheets consisting of two oxygen or hydroxyl layers parallel to one another in which the cation is embedded (Figure 1b). If aluminum is the cation present in the lattice, this layer is referred to as the alumina or gibbsite sheet, whereas if magnesium is the metal center, the layer is called the magnesia or brucite sheet. In order to maintain electro-neutrality within the lattice, only two-thirds of the total sites need be filled if aluminum serves as the metal cation. All lattice sites must be filled if magnesium is the metal center.

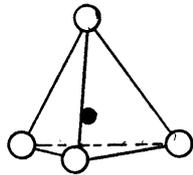
The other basic unit consists of silicon tetrahedrally coordinated to four oxygen atoms (Figure 1c). By sharing the oxygen's comprising the base of the tetrahedron with one another a hexagonal network is formed, which is repeated indefinitely, forming a silica sheet (Figure 1d).



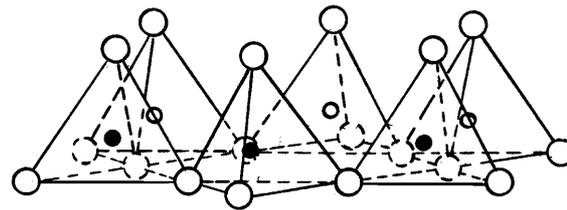
(a) Aluminum or magnesium octahedron



(b) Alumina or magnesia sheet



(c) Tetrahedral orthosilicate unit



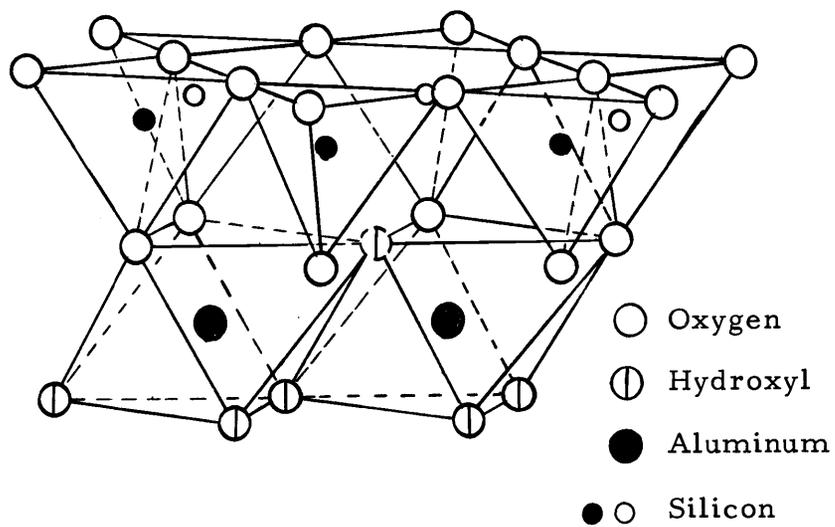
(d) Silica sheet

Figure 1. Structural units of clay minerals.

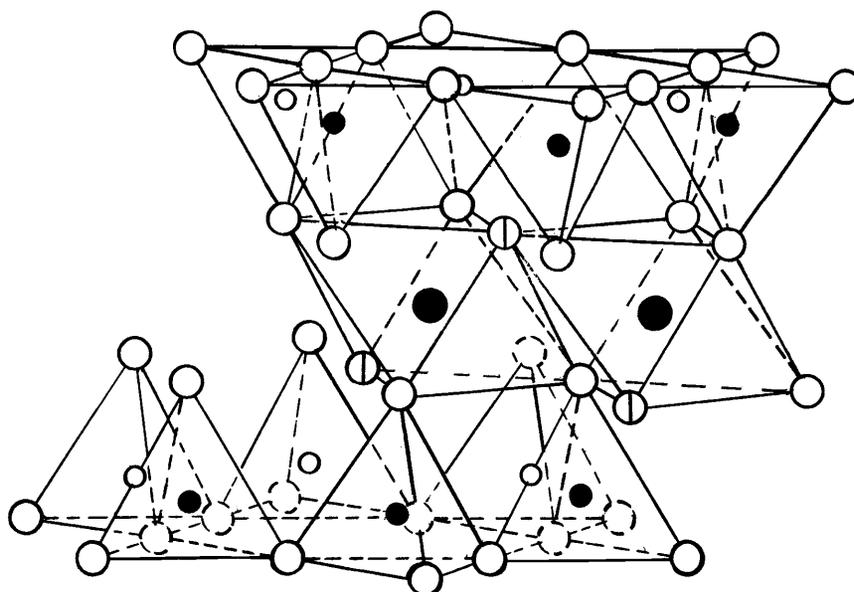
These two fundamental sheets are added together to form two and three layer clay minerals. In two layer minerals, such as kaolinite, an alumina or magnesia layer is combined with a silica layer. By sharing the active oxygens of the silica sheet with the octahedral sheet, a common layer is formed. In this common layer those ligands shared with aluminum and silicon atoms are oxygen while the remaining ligands of the octahedral sheet are hydroxyl groups. This structure is represented in Figure 2a.

Montmorillonite, a three layer mineral (Figure 2b) and the dominant clay mineral component of bentonite, is composed of two silica tetrahedral sheets with an alumina octahedral sheet inserted between. The tips of the silica tetrahedra all point in the same direction--toward the center of the unit. As in the two layer minerals the active oxygens of the silica layers are shared with the octahedral sheet.

In the horizontal plane (the a and b axes) these platelets are continuous for both two and three layer minerals and are stacked one above the other in the vertical direction. A three layer mineral whose platelets are composed of an alumina sheet and two silica sheets in which no lattice vacancies or substitutions occur is pyrophyllite. It is found that the distance between aluminum atoms of different platelets stacked one above the other (the 001, basal or c-spacing) is about a minimum of  $9.2 \text{ \AA}$  for these three layer clays and about  $7.1$



(a) Kaolinite



(b) Montmorillonite

Figure 2. Structure of Kaolinite and Montmorillonite.

to  $7.2 \text{ \AA}$  for two layer minerals.

The formula for pyrophyllite is  $(\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20}$ . Lattice vacancies and lattice substitutions cause montmorillonite to differ from this theoretical value. Substitution may take place in either the silica or alumina layer. For instance, aluminum or phosphorus may replace silicon in the tetrahedral sheet and/or magnesium, iron, zinc, nickel, or lithium, etc. may replace aluminum in the octahedral sheet. In the tetrahedrally substituted layer replacement of silicon is observed not to exceed 15% whereas replacement of aluminum varies from a few to all.

Because of these cation substitutions a net negative charge arises within the lattice. Consequently, cations populate the surfaces between platelets as well as their edges. These cations may be either organic or inorganic in nature and their presence has a profound effect on the characteristics of the mineral. Due to the fact that these cations reside in the space between platelets they are readily replaced, and are, therefore, referred to as the exchangeable cations. Montmorillonite possesses a cation exchange capacity (C. E. C.) of between 80 and 150 milliequivalents/100 grams.

#### Characteristics of Montmorillonite

The outstanding feature of the montmorillonite structure is that the lattice is able to expand in the vertical direction. This occurs

when water and other polar molecules enter between the platelets. Consequently, the c-axis dimension is not fixed but varies from  $9.6 \text{ \AA}$ . Studies in vapor phase adsorption by Bradley, Grim and Clark (13) suggest that hydration takes place in a stepwise fashion. That is to say, the interlamellar water layer is one, two, three, or four layers thick. It has been hypothesized that the mechanism involves two steps. Initially, the exchangeable cation is hydrated, then adsorption occurs on the remaining oxygen surface. Whether or not the forces involved in this adsorption process are conducive to hydrogen bonding of water to the oxygen surface of the clays, is a point of contention. Anderson (3) and others (19) have determined that water closest to the mineral surface is highly disordered and mobile, presumably, due to the competing electrical forces at the interface. More recently, Farmer and Russell (18) in an infrared study concluded that water is only very weakly hydrogen bonded to the silicate surface. Also, findings of Leonard (32) indicate that at low water contents, the exchangeable cation exerts the dominant force in determining the structure of the adsorbed water, not the mineral surface. As much as 0.5 g water/g clay may be taken up in this adsorption process. When montmorillonite is exposed to water in the liquid state, the c-axis may expand to  $100 \text{ \AA}$  or more, adsorbing as much as 10 g water/g clay. The result is the formation of a gel.

Water is not the only species that will be adsorbed by

montmorillonite. A study of adsorption from the gas phase (7), involving various polar and non-polar molecules on sodium rich montmorillonite has shown that only the polar molecules are intercalated. Consequently, various organic molecules with significantly large dipole moments would be expected to be adsorbed between platelets, replacing water. It has been postulated that the polar organic molecules solvate the exchangeable cation in a fashion analogous to that of water and induced dipole-induced dipole interactions between the methylene groups and the silicate surface occur. Farmer and Mortland (17) in 1965 confirmed that gaseous ethylamine adsorbing onto Cu-montmorillonite completely displaced the coordinated water. Formation of a square-planar copper-ethylamine complex was indicated by infrared and x-ray spacing evidence. A decrease in nitrogen content over a period of two days was ascribed to the loss of interlayer ethylamine which was not complexed.

The exchangeable cation has a profound influence upon the characteristics of montmorillonite. When an inorganic clay is exposed to organic cations such as a quaternary ammonium salt, cation exchange takes place. The  $R_4N^+$  cation becomes attached to the exchange site through the nitrogen end. Van der Waals forces between the carbon chains and the oxygens of the silicate surface further secures the cation. Selectivity of adsorption is transformed from polar to non-polar adsorbates. When only partial exchange occurs, the adsorptive capacity for

non-polar molecules such as benzene or n-heptane rises in proportion to the fraction of inorganic cations replaced (4). A thermodynamic comparison was made of intercalation on non-polar adsorbates by a short-chain organic exchangeable cation, on the one hand, and a long-chain organic chain, on the other (5, 6). Intercalation was very exothermal in the short-chain organo-clay, as would be expected if the hydrocarbons and other non-polar adsorbates were inserted into permanent gaps between the laminae. In the long-chain organo-clays, prior to swelling, the cations fill the interlaminar space, so that adsorption involves swelling and a process of mixing of adsorbate molecules with the long carbon chains of the cation. Consequently, this involves small heats, sometimes endothermic, and a positive entropy of mixing.

#### Selective Adsorption from Binary Solution

Four major factors are important when considering adsorption from the liquid phase onto a solid (21). They are: (a) the thickness of the adsorbed film, (b) the orientation of the adsorbed molecules, (c) the polarity of the solid surface and adsorbate, and (d) the interaction between liquid components. Consequently, due to the degree of complexity of adsorption from solution, relatively little has been done.

Not until the 1920's was selective adsorption from a binary solution investigated. Composite isotherms in which the apparent

adsorption of solution versus the pre-equilibrium concentration, described the selectivity of an adsorbent for both components, A and B, of a binary mixture. The isotherm is usually "S" shaped. Initially, at low concentrations of component A, the apparent adsorption is positive. As the quantity of A increases in solution, the apparent adsorption decreases, finally becoming negative. The apparent adsorption is only a relative measure. A positive value of A indicates that the adsorbed phase is richer in that component than is the bulk liquid and vice versa. That value of the mole fraction, where the apparent adsorption changes from positive to negative, is equivalent to the concentration of the two components in the adsorbed phase.

While the change in composition of a liquid mixture is readily discerned there is no direct approach for determining the total amount adsorbed, unless assumptions are made. Barrer and Perry (8) pointed out that adsorption isotherms of mixtures cannot, in general, be obtained from those of the individual components, but that selective adsorption from mixtures can only be studied by working directly with the mixtures. Consequently, very few studies have been made of adsorption from binary solutions by montmorillonite when both components are strongly adsorbed. Nevertheless, Heydemann and Brindley (28), by observing the change in composition of the liquid mixture combined with the weight of material adsorbed by the

clay, were able to determine the individual isotherms of n-alkyl alcohol-bromide mixtures selectively adsorbed by inorganic cation exchanged montmorillonites. Molecules with OH and Br as functional groups were chosen because the alcohol is potentially capable of hydrogen bonding to the silicate surface whereas the bromides are likely to adsorb by cation-dipole interactions. From this investigation it was concluded that adsorption of the alcohol arose from predominantly hydrogen bonding while a decrease in adsorption of the bromides with increasing chain length was regarded as being consistent with a cation-dipole mechanism.

A special case of selective adsorption from binary solutions arises when a polar component is dissolved in a non-polar solvent. This approach was employed by Greene-Kelly (23). Under the assumption that only the polar component was adsorbed, the adsorption isotherm of pyridine on Na-montmorillonite from pyridine-cyclohexane solutions was determined. However, it cannot be assumed in all cases that a non-polar solvent, which is not adsorbed when alone, will not be adsorbed when in solution with a polar adsorbate. Hiltner (21) observed that heptane did not expand the platelets of alkylammonium montmorillonites, but was extensively adsorbed when a polar component had been preadsorbed.

More recently, Bissada, Johns, and Cheng (12) studied the adsorption isotherms of ethanol and acetone on K, Na, Ba, and

Ca-montmorillonite from solutions in dodecane. The objective of this investigation was to determine whether or not the dominant mechanism in the adsorption of alcohol was due to hydrogen bonding with the surface oxygens or cation-dipole forces. In contrast to the paper discussed previously by Heydemann and Brindley, they concluded that cation-dipole interactions dominate the adsorption process. Dowdy and Mortland (16) arrived at a similar conclusion. Calculated theoretical values for the electrostatic attractive energies between the respective cations and molecules (12) agreed with experimental values determined by Bissada and Johns (11).

The determination of surface area from solution adsorption studies has been attempted, although vapor or gas adsorption is a more common approach. A primary condition is that a complete monolayer forms. Although the degree of coverage may be referred to as the formation of a monolayer, it does not necessarily imply that a close-packed layer of single molecules exists. This layer may (a) contain solvent as well as solute molecules, (b) consist only of isolated clusters adsorbed on the most active sites, or (c) consist of ionic micelles, either packed closely or well separated (22). Fu, Hansen, and Bartell (20) observed that a monolayer of butyric acid adsorbed on carbon from water contained solvent. Only if a definite adsorption model is obeyed and a closed packed layer of single molecules is present can specific surface area determinations readily be made.

Usually, this limits surface area determinations to adsorption studies where the simple Langmuir equation for monolayer adsorption is applicable. Smith and Hurley (36) employed this mathematical formulation in determining the surface area of carbon blacks from a solution of fatty acids dissolved in water. Nevertheless, Hansen et al. (26) observed that a number of higher acids and alcohols in aqueous solution adsorbed on carbon in a multilayer fashion. Consequently, they employed the B. E. T. equation in determining the surface area. Bartell and Donahue (9) in a similar investigation observed that the surface area varied with the solvent employed. Thus, surface area determinations by means of solution adsorption, while convenient experimentally, cannot be considered reliable.

## EXPERIMENTAL

Apparatus

To determine the small concentration changes due to the selective adsorption process, variations in the refractive index of the binary solution were observed. Others (21, 31) have employed this procedure previously. Heydemann and Brindley (28) utilized a Zeiss Abbe refractometer to determine the selective adsorption of n-alkyl alcohol-bromide mixtures by montmorillonite. In this investigation it was not necessary to measure the refractive index directly, but to measure the difference in refractive index between the initial concentration of the binary solution and its concentration once adsorption onto the clay had ceased. Consequently, a differential refractometer was utilized.

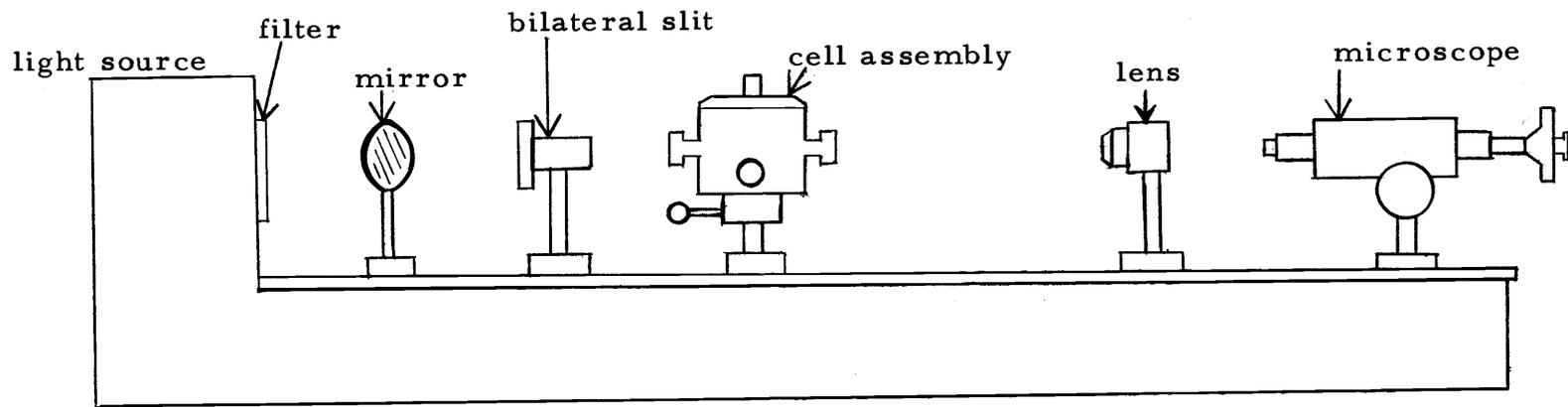
The differential refractometer was selected basically because it is about a hundred times less sensitive to temperature changes when compared to a normal refractometer. Hence, one is able to measure refractive index changes to six decimal places instead of four. Secondly, the differential refractometer is able to compare samples directly. Therefore, these concentration changes can be determined by a single reading.

The instrument employed was a Brice-Phoenix model BP-2000-V

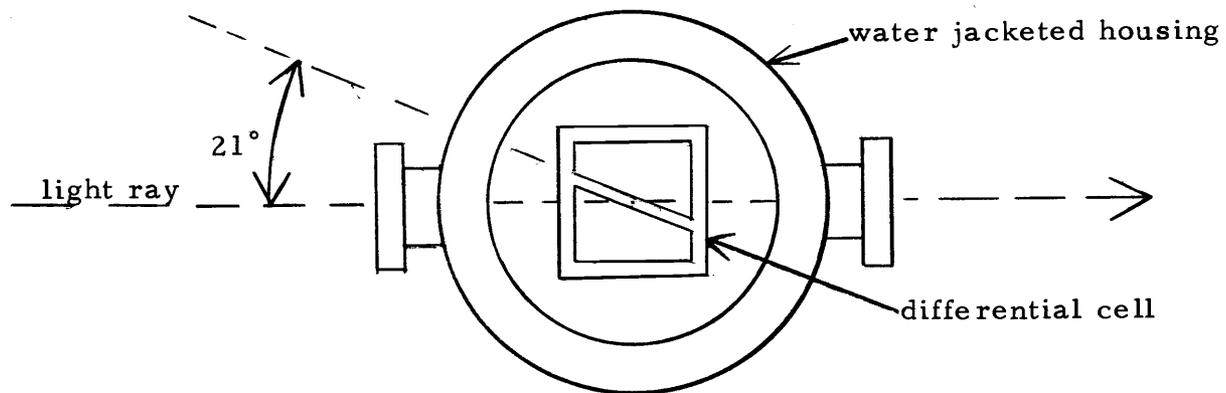
differential refractometer (Figure 3a). It comprised a mercury vapor lamp, type AH-3, and a blue filter to isolate the 436 nm wavelength; a semitransparent mirror for utilizing other light sources; a bilateral spectrometer slit; a water jacketed housing maintained at  $25 \pm 0.1^\circ \text{C}$  containing an optical glass differential cell; a projection lens; and a microscope with traveling cross-hair. The partition which divided the cell into two compartments formed an angle of  $21^\circ$  with respect to a light ray traversing it (Figure 3b). In order to inhibit evaporation while taking a reading, a brass plate was cemented onto the top of the cell with epoxy adhesive. Two capillary tubes per cell half were soldered onto this brass plate in order that solution could be added or removed from each compartment, separately. The instrument was calibrated in hundredths of a millimeter, where  $0.01 \text{ mm} = 0.000018$  refractive index difference, and differences in the refractive index up to about 0.01 could be measured.

#### Clay Materials and Reagents

The adsorbent employed in this investigation was Ion Exchanged Centrifuged Wyoming Bentonite produced by the Baroid Sales Division of the National Lead Company. This ion-exchanged Na-bentonite was converted to its  $\text{NH}_4$ , Ca, and Ba counterparts by means of a cation exchange column. Amberlite I. R. 120 served as the cation exchange resin. So as to assure 100% conversion 0.3% and 0.5% by weight



(a) Differential refractometer



(b) Cell assembly  
(Top view)

Figure 3. Apparatus.

solutions of Na-bentonite were passed through the column at a rate of ten milliliters per minute (33). The more dilute, 0.3%, solution was employed in converting to the divalent cation forms due to the fact that these forms flocculate more readily. In order to concentrate the  $\text{NH}_4$ -bentonite solution, it was vacuum distilled at 35° C. With the aid of a vacuum oven, the remaining water was removed. The divalent bentonite solutions were boiled until all water was driven off. The clays were then hand ground to 200 mesh.

To assure approximate equivalent water content in the various bentonite forms, the Na, Ba, and Ca clays were dried in an oven at 110° C for one hour.  $\text{NH}_4$ -bentonite was dried in a vacuum oven at 35° C for 24 hours. The clays were then stored over anhydrous calcium chloride until needed.

Methanol and ethanol were employed as the polar components of the liquid mixture. Toluene functioned as the non-polar component. All solvents were of reagent grade.

### Procedures

In terms of the analytical procedure, one of the fundamental problems that had to be overcome was the variation in concentration of the binary solution due to evaporation or adsorption of water from the atmosphere. To alleviate this difficulty the samples were sealed in glass vials of varying sizes, depending on the quantity of solution

and adsorbent present. Seventeen millimeter Pyrex glass tubing was utilized in making test tubes of 15, 20 and 25 centimeters in length, accommodating 10, 15, and 20 milliliters of solution, respectively.

Although only about 1.5 ml of solution were required for the analysis, a minimum of five milliliters were necessary for washing each compartment of the cell assembly. Therefore, at least ten milliliters of solution per sample were required. Moreover, because this investigation dealt with low concentrations of the polar component (i. e., mole fractions from 0.010 to 0.140), larger quantities, at times, of solution (15 or 20 ml) were necessary in order to decrease the error in making them. Because of this greater amount of solution, larger quantities of bentonite were also added.

In order to facilitate sealing after the clay and liquid mixture were added, the ends of the tubes were drawn out. Due to the sensitivity of this analysis to extraneous water, the newly made vials were exposed to 110° C environment for one hour. They were then stored over anhydrous calcium chloride or in a vacuum until needed.

Four hundred and 800 milligrams of the homionic bentonite were weighed out to 0.1 milligrams and placed into 15 and 20, or 25 centimeter vials, respectively. In adding the proper quantity of alcohol and toluene to each sample, two microburettes were utilized. During this process, the test tubes were immersed in a dewar

containing acetone and dry ice in order to inhibit evaporation. Immediately after the solvents were added, the vials were sealed with a torch. Three samples at each concentration were made so as to insure reproducibility. The concentrations, expressed in terms volume-volume percent, were recalculated in terms of mole fraction. Standards were made in a similar fashion.

To disperse the homionic bentonite throughout the liquid mixture, the ampoules were shaken for one hour. They were then placed in a thermostated water bath at  $30^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ , where they remained for a minimum time of 24 hours, in order to assure that equilibrium had been attained.

Once equilibrium had been achieved, the sealed ampoules were ruptured at the "drawn out" portion, which was encased in a rubber tube in order to prevent evaporation during the transfer process. A syringe was utilized in transferring the supernatant from the vial to one of the compartments of the refractometer cell assembly. During this procedure, it was observed that adsorption occurred onto the walls of the cell. Consequently, when the next sample was added, desorption took place and the solution was significantly altered. Hence, it was necessary to wash the compartment three times prior to continuing.

The procedure was to add a standard to both compartments of the cell assembly. In order to inhibit evaporation the capillary tubes,

fixed to the brass plate which covered the top of the refractometer cell, were then capped. After allowing five to ten minutes for thermal equilibrium to be attained, a measurement was recorded. Because it varied (a characteristic of the apparatus) this "zero" reading was required at each concentration value. Leaving one of the compartments sealed, the other was opened and the standard was removed with a syringe. After washing the compartment, the supernatant was added; the capillary tubes were resealed; and a reading was recorded after allowing the solution to come to thermal equilibrium with the cell assembly. The difference between the "zero" and final reading was related to the change in concentration due to the selective adsorption process.

By varying the concentration of the standard in one compartment and leaving the same standard in the other compartment, the relationship between refractive index and concentration was discerned. It was found to be linear. The conversion factor was expressed in terms of moles of alcohol per mole of toluene. This value was equivalent to one unit (0.01 mm) on the differential refractometer.

## EXPERIMENTAL RESULTS AND INTERPRETATIONS

Data were acquired in the low alcohol concentration region of the binary mixture. The partial composite isotherms obtained are shown in Figures 4 and 5. A plot of  $n\Delta x/m$  versus  $x$  is a measure of the adsorption selectivity by various homionic bentonites, where  $n$  is the total number of millimoles of solution,  $\Delta x$  is the change in mole fraction of the polar component,  $m$  is the mass of adsorbent in grams, and  $x$  is the mole fraction of alcohol in bulk solution prior to adsorption. A positive value of  $n\Delta x/m$  indicates a preference for adsorption of alcohol while a negative value would be suggestive of preferential adsorption by toluene. As can be seen from the data, the alcohol is selectively adsorbed. This can be explained in terms of the organophobic nature of the clay. As in gas-phase adsorption studies, the polar species would be expected to be intercalated.

From this investigation it was concluded that for the ethanol-toluene adsorption studies the order of decreasing adsorption relative to a given homionic bentonite was  $\text{Ca}^{2+} > \text{Ba}^{2+} > \text{Na}^+ > \text{NH}_4^+$ , and that for the methanol-toluene system was  $\text{Ca}^{2+} > \text{Ba}^{2+} \sim \text{Na}^+ > \text{NH}_4^+$ . In comparing the two binary mixture adsorption studies, it is apparent that less error is observed when ethanol functions as the polar component. Evidently, the precautions taken in terms of the technique to discourage evaporation were not as effective in the case of the

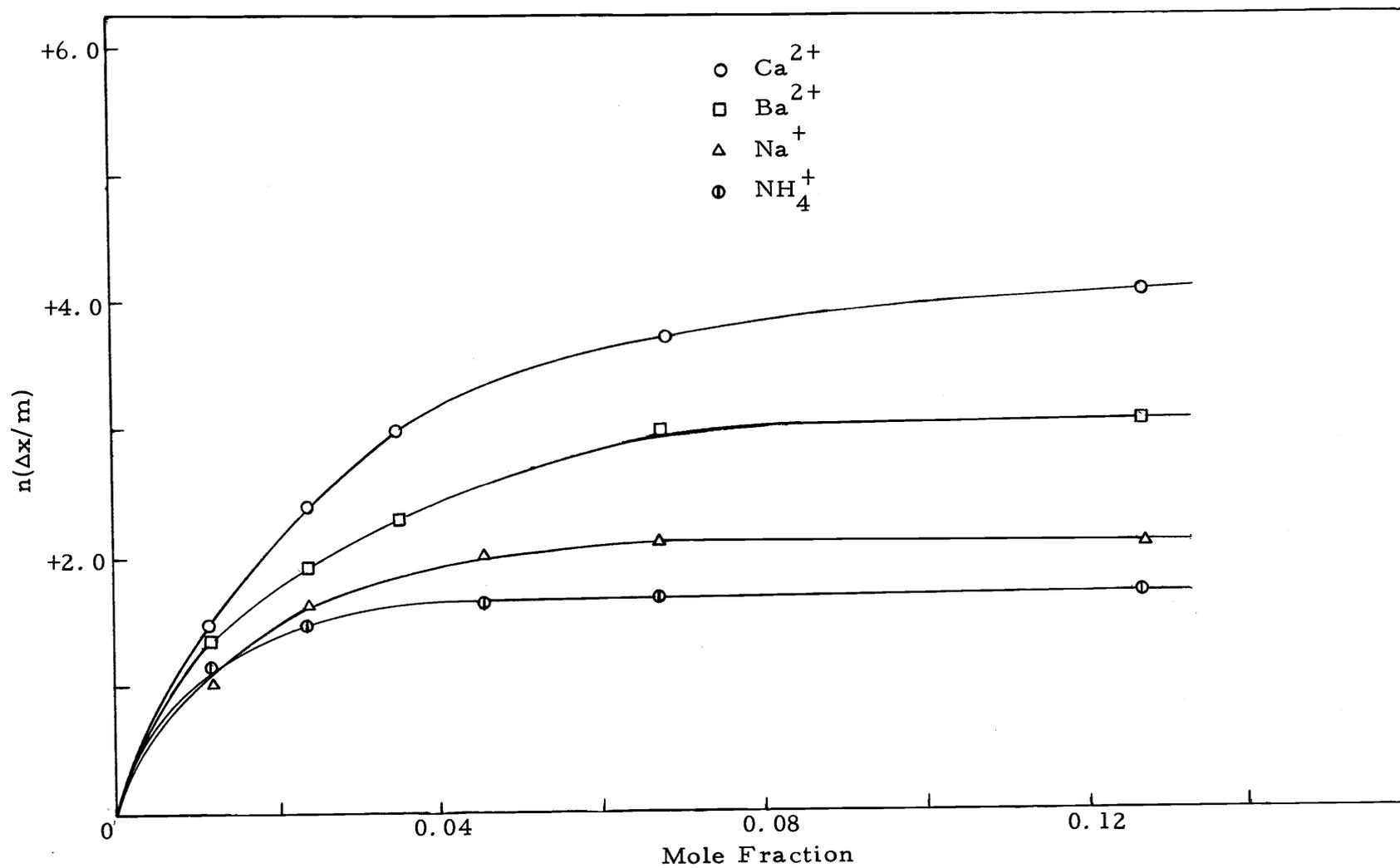


Figure 4. Adsorption of Ethanol-Toluene Solution on Homionic Wyoming Bentonite.

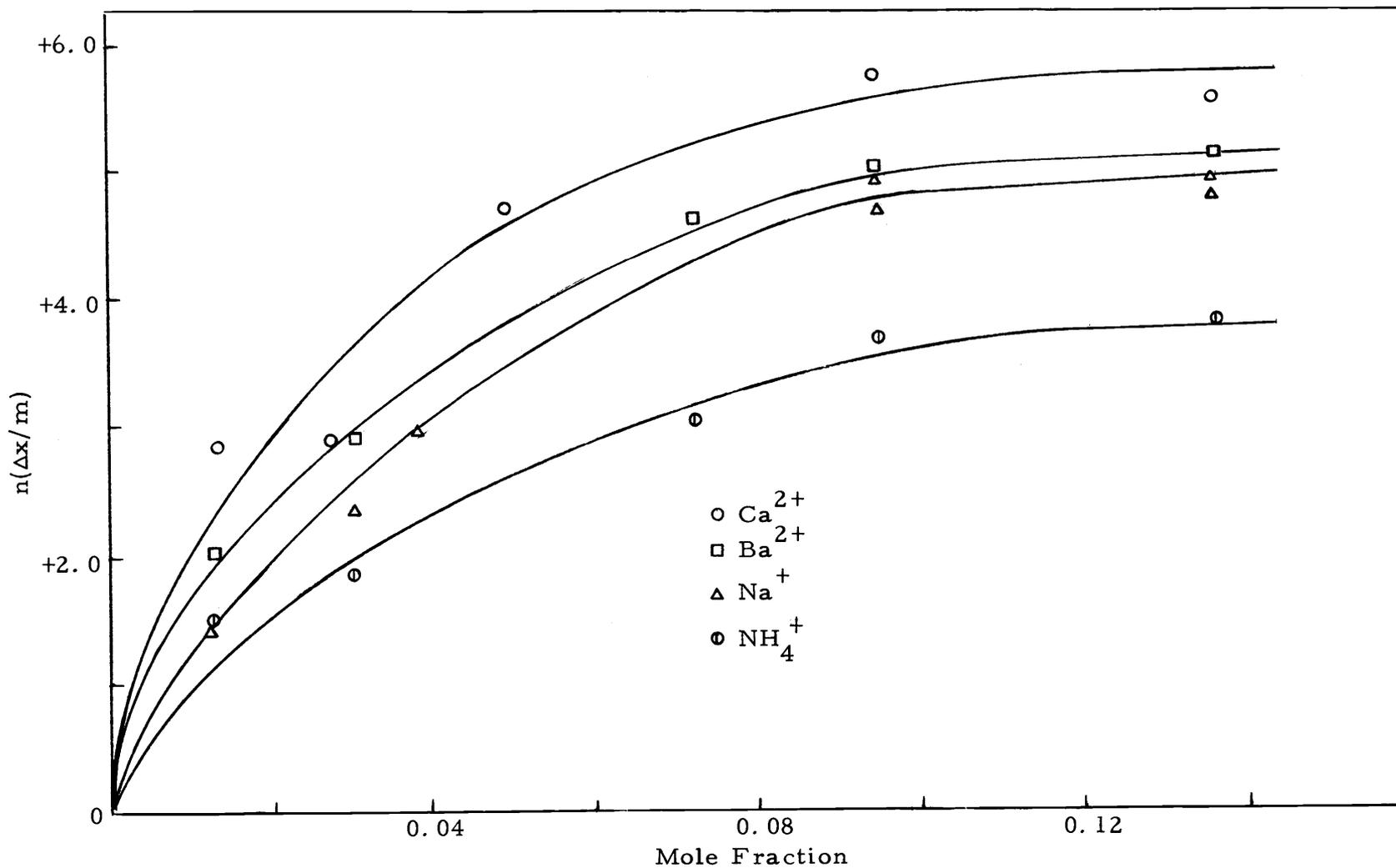


Figure 5. Adsorption of Methanol-Toluene Solution on Homionic Wyoming Bentonite.

methanol-toluene mixtures. This can be attributed to the significantly higher vapor pressure of methanol.

The ionic potential, which is the ratio of charge to radius, is a qualitative measure of the electrostatic field surrounding an ion.

Values of the ionic potential are listed in the following.

Table 1. Ionic potentials of various cations

Cation	Radius	Ionic Potential
$\text{Ca}^{2+}$	0.99 Å	2.02
$\text{Ba}^{2+}$	1.35	1.48
$\text{Na}^+$	0.95	1.05
$\text{NH}_4^+$	1.43	0.70

Referring to this table, it can be seen that relative to a given cationic bentonite, the ionic potential varies in the same manner as the degree of adsorption. This suggests that at least at low mole fractions of alcohol, the dominant mechanism of selective adsorption is the solvation of the exchangeable cation by the polar component, and that the degree of solvation can be associated with the intensity of the electrostatic field surrounding this cation. Others (12) employing a similar system have reached the same conclusion.

Secondly, it was observed that for a given homionic bentonite methanol adsorbed to a greater extent than ethanol. Assuming a

solvation mechanism, that species which aligns more readily in the electrostatic field of the exchangeable cation would be expected to adsorb to a greater degree. Alignment in a field is dependent upon the size of the molecule as well as its dipole moment. A measure of this alignment in a field is the dielectric constant. The dielectric constants at 25°C are 24.3 and 32.6 for ethanol and methanol, respectively. Consequently, from these values, one would anticipate the results observed. Thus, from the data it can be concluded that cation-dipole interactions of an electrostatic nature play a significant role in the selective adsorption process.

The fact alone that methanol adsorbs to a greater extent than ethanol can not be used as support for discriminating between two possible mechanisms. If one assumes that the mechanism is one involving adsorption onto the silicate surface, one would also expect the results observed when considering the size alone of the polar species. Only the fact that the degree of adsorption significantly varied when the exchangeable cation was varied can be employed to support a solvation mechanism. This does not, however, imply that adsorption onto the silicate surface is not occurring at the same time.

## APPLICABILITY OF THE B. E. T. EQUATION

In a similar adsorption study, concerning a binary mixture of methanol-toluene selectively adsorbed by Na-hectorite, Hanson (27) observed that only the polar component was intercalated. Secondly, from the shape of the isotherm it appeared that adsorption was multilayer in nature. In addition, measurements of (001) spacings by an X-ray diffractometer involving flakes of Na-bentonite sprayed with a 100% ethanol solution also indicated that adsorption was multilayer. Consequently, assuming that only the polar species was selectively adsorbed in our investigation, the non-polar component, toluene, might be looked upon as an inert material which merely occupied space. Hence, it was speculated that our system might be analagous to gas-solid multilayer adsorption. Therefore, those mathematical models describing gas-solid multilayer adsorption might be applicable.

Bartell and Donahue (9) utilized the B. E. T. equation for multilayer gas-solid adsorption in order to interpret the adsorption isotherms of water by silica gel from binary solutions of higher alcohols and water. Assuming that  $n$ , the number of layers adsorbed onto the solid surface is large (i. e., greater than four or five), the following form of the B. E. T. (Brunauer-Emmett-Teller) equation may be employed.

$$X/V(1-X) = 1/V_m C + (C-1)X/V_m C$$

With respect to this equation  $X$  = the reduced pressure,  $p/p_0$ ;  
 $V$  = the volume of gas adsorbed per unit area;  $V_m$  = the volume of a monolayer; and  $C$  = a constant. A plot of  $X/V(1-X)$  versus  $X$  should be linear. From the slope and intercept one is able to determine the two parameters  $V_m$  and  $C$ .

In their calculations, the variable  $V$  (the volume of gas adsorbed per unit area) in the B. E. T. equation was replaced by the number of moles of water adsorbed per gram,  $x/m$ . Moreover, in the case of solution adsorption the rational parameter for  $X$  was chosen to be the reduced concentration,  $c/c_0$ . From the slope and intercept of the B. E. T. plot the number of moles of water associated with a monolayer and the constant  $C$  were determined. More recently, Akulich and Starobinets (2) employed the B. E. T. equation to describe water adsorption from water propanol solutions by anion-exchanger Dowex 1X8 in various forms. In their calculations the correlating parameter for  $X$  was the activity of water in solution,  $a_w$ .

In our calculations the reduced concentration,  $c/c_0$  was an unacceptable correlating variable for  $X$ . Moreover, attempts employing the activity of alcohol in solution proved unrewarding. Consequently, the mole fraction of alcohol present in the binary mixture,  $x$ , was used. Secondly, the variable  $V$  was replaced with its adsorption from solution counterpart,  $n_a/m$ , the number of millimoles of alcohol adsorbed per gram.

Before proceeding with the B. E. T. plot, the values of  $n_a/m$  at various concentrations had to be determined. Under the assumption that toluene was not intercalated, this was accomplished by converting the composite isotherms to their individual alcohol adsorption isotherms utilizing the relationship (1)  $\frac{n\Delta x_a}{m} = \frac{(n_a x_t - n_t x_a)}{m}$ . With respect to this relationship  $n_a$  and  $n_t$  are equivalent to the number of millimoles of alcohol and toluene adsorbed onto the surface, respectively, while  $x_a$  and  $x_t$  represent the mole fractions of alcohol and toluene in solution at equilibrium, respectively.

The B. E. T. equation was used in the low alcohol concentration region of the isotherms (i. e., from 0.010 to 0.140 mole fraction of alcohol). Values for  $n_a/m$  were taken at successive 0.005 mole fractions except for the ethanol  $\text{NH}_4$ -bentonite system where 0.002 intervals were utilized. Within a limited range of concentration the plot appeared linear. The region of linearity was greatest for the methanol Na-bentonite adsorption isotherm (i. e., from 0.045 to 0.125) whereas it was least for the ethanol Na-bentonite system (i. e., from 0.015 to 0.055). From the slope and intercept of the B. E. T. plot the values for  $V_m$  and  $C$  were calculated. Table 2 gives a listing of these values.

It was observed that  $V_m$  increases as one varies the exchangeable cation in the order  $\text{NH}_4^+ < \text{Na}^+ < \text{Ba}^{2+} < \text{Ca}^{2+}$  when ethanol is selectively adsorbed whereas when methanol is utilized as the polar

Table 2. Calculated\* values from the B.E.T. equation.

Cation	Alcohol	Region of Linearity (mole fraction of alcohol)	$V_m$ (millimoles per gram)	Molecules per Cation	C	$E_1 - E_2$ (Kcal. /mole)
$\text{NH}_4^+$	Ethanol	0.034-0.085	1.7	1.8	540±140	3.78±0.17
Na <sup>+</sup>	Ethanol	0.015-0.055	2.8	3.0	51±4	2.36±0.05
Ba <sup>2+</sup>	Ethanol	0.030-0.075	4.1	8.9	33±5	2.10±0.10
Ca <sup>2+</sup>	Ethanol	0.045-0.110	4.6	10.0	50±7	2.25±0.09
$\text{NH}_4^+$	Methanol	0.040-0.110	5.2	5.7	16±1	1.66±0.04
Na <sup>+</sup>	Methanol	0.045-0.125	6.5	7.1	18±2	1.74±0.06
Ba <sup>2+</sup>	Methanol	0.030-0.105	6.5	14.1	31±3	2.00±0.06
Ca <sup>2+</sup>	Methanol	0.035-0.105	7.0	15.2	37±6	2.17±0.10

\* Calculations are based on data possessing a relative error of 3% and 5% for the adsorption isotherms of ethanol-toluene and methanol-toluene, respectively.

component the order of increasing  $V_m$  is  $\text{NH}_4^+ < \text{Na}^+ \sim \text{Ba}^{2+} < \text{Ca}^{2+}$ .

Moreover, for a given homionic bentonite, this numerical quantity was greater when methanol functioned as the polar species. Consequently,  $V_m$  was interpreted as being the number of millimoles of alcohol associated with solvation of the exchangeable cation.

If the cation exchange capacity (C.E.C.) of the homionic bentonite is known, the number of alcohol molecules associated with a single exchangeable cation can be determined by utilizing the values for  $V_m$ . The C.E.C. of this univalent homionic bentonite is 92 meq/100g. From this information one obtains values of 3.0, 8.9, and 10.0 molecules of ethanol per cation for Na-, Ba-, and Ca-bentonite, respectively. Bissada et al. (12) employing ethanol-dodecane mixtures selectively adsorbed by homionic montmorillonite determined that 3, 8, and 10 molecules of ethanol were associated with a single exchangeable cation in Na-, Ba-, and Ca-montmorillonite, respectively.

It is important to elaborate upon this numerical quantity the number of molecules of alcohol per cation. The number of molecules per cation may be misleading in that whole numbers might be anticipated. But solvation of the exchangeable cation in this case is dependent upon the nature of the electrostatic field present. It is found that the intensity of this field depends on whether the charge deficiency arises in the octrahedral or tetrahedral site (30). Secondly, the

distribution of cations is probably not uniform so that spatial considerations may govern the size of a given solvation sphere. Moreover, it has been observed that water in the interlaminar spacings is mobile (19), suggesting that a quasi-liquid state may exist. Consequently, this numerical quantity should be interpreted as being merely an average.

The constant  $C$ , determined from the B. E. T. plot, is related to the difference  $E_1 - E_2$  where  $E_1$  represents the heat of adsorption of the first layer and  $E_2$  is representative of the heat of adsorption of all subsequent layers. According to the B. E. T. equation

$$C = (a_1 b_2 / a_2 b_1) \exp. \frac{E_1 - E_2}{RT}$$

where  $a_1$  and  $b_1$  are constants associated with the first layer of adsorption and  $a_2$  and  $b_2$  are constants associated with all subsequent layers of adsorption. From the nature of these constants the pre-exponential ratio is approximately unity (15). Therefore,  $-E_1 - E_2 = RT \ln C$  where  $T$  is the temperature in degrees Kelvin, and  $R$  is the gas constant in cal./deg.-mole.

Due to the fact that most of the forces were satisfied by wetting of the solid by bulk solution and by the adsorption of the first layer, the term  $E_2$  for adsorption from solution should be small. This suggests that the quantity  $E_1 - E_2$  is approximately equivalent to  $E_1$  and is therefore in this case, a measure of the solvation energy of the exchangeable cation by the alcohol. Referring back to Table 2, in some cases the energy difference  $E_1 - E_2$  is greater when ethanol serves as the adsorbate. This is contrary to what one would anticipate.

According to Benson and King (10) the theoretical attractive energy between an ion and a polar molecule  $\phi_p$ , can be determined from the expression

$$\phi_p = - \frac{C_a^+ \cdot u_p}{r_o^2}$$

where  $C_a^+$  is the charge of the cation,  $u_p$  is the dipole moment of the polar molecule, and  $r_o$  is the interaction distance, taken as the distance from the center of the cation to the center of the alcohol dipole. The dipole moments of methanol and ethanol are of approximately equivalent magnitude. Therefore, the interaction distance,  $r_o$  should determine the relative difference in the electrostatic attractive energy involving the two polar molecules. Consequently, the inverse relationship between energy and interaction distance should lead one to conclude that solvation by methanol exhibits a greater attractive energy.

Hence, one can only speculate concerning this discrepancy. It may be that the term  $E_2$  is not small and may effect this energy difference in such a manner so as to acquire the observed values. More likely, the error in determining the constant  $C$  can be quite large at times, thus rendering it a useless parameter in making interpretations. In addition, the applicability of the B. E. T. equation to this solution adsorption study may be "more apparent than real." The plot was linear in a very small concentration range, less than

nine percent of the complete isotherm. Also, if one varied the shape of the isotherm in the region where linearity was expected, one always observed some concentration range in which the plot was linear. This may suggest that in this case the B. E. T. equation is not sensitive to multilayer solution adsorption but merely sensitive to a certain characteristic shape of isotherm to which this solution adsorption study followed.

## SUMMARY

This investigation dealt with a special case of selective adsorption from binary solutions in which a polar component, ethanol or methanol, was dissolved in a non-polar solvent, toluene. Data were acquired in the low alcohol concentration region of the composite isotherms. The results were explained in terms of the ionic potentials of the exchangeable cations and the dielectric constants of the two alcohols. A solvation mechanism was proposed in which cation-dipole interactions of an electrostatic nature were dominant.

Under the assumption that toluene was not intercalated and adsorption was multilayer in nature, applicability of the B. E. T. equation for multilayer gas-solid adsorption was investigated. The B. E. T. plot appeared linear in a small concentration range.  $V_m$  was interpreted as being the amount of alcohol required to solvate the exchangeable cation. Although values calculated for the heats of adsorption were contrary to those anticipated, values for  $V_m$  agreed reasonably well with data obtained from other studies. Consequently, the B. E. T. equation was found not to be totally applicable, but to a first approximation and within a limited concentration range it was useful in describing this type of adsorption system.

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