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Title: SOLVENT SELECTIVITY BY AN ORGANOClay COMPLEX

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The selective adsorption from a series of binary solutions on an organoclay complex has been studied in relation to the gelling ability of this organoclay. Adsorption isotherms were obtained for a series of polar organic solvents in toluene. The isotherms were of the usual "S" or "U" type depending upon the polar component. The crossing point in which the concentration of the binary solution did not change due to selective adsorption was assumed to be the concentration of the adsorbed phase.

The ability for the polar component to adsorb was interpreted in terms of three properties of that polar component: size, dielectric constant and its association with the hydrocarbon. It was found that a relationship can be determined between the concentration of the polar component in the adsorbed phase and the gel strength. A model was proposed for the structure of the gel based on the adsorption of the polar component.
Solvent Selectivity by an Organoclay Complex

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SOLVENT SELECTIVITY BY AN ORGANOCLAY COMPLEX

INTRODUCTION

**Definition and Origin of Clays**

The term clay has been given a variety of meanings depending upon the context in which it is used. In general it may be defined as a natural, earthy, fine-grained material which develops plasticity when mixed with limited amounts of water. The geologist has used the term clay to describe the grade of a material finer than four microns. In soil science, however, the tendency has been to use two microns as the upper limit of the clay size grade. The term as used in chemistry and as used in this paper refers to a finely divided crystalline material having a particular crystalline structure which will be described later.

Clay minerals are produced by several means. They may be brought about naturally by hydrothermal actions and are found associated with hot springs, geysers, or fumaroles. Natural occurrence in the soil has also been attributed to weathering of rocks. They may also be found in ocean, lake or river sediments or in glacial deposits. All of the clay minerals with the exception of attapulgite-sepiolite and halloysite have been produced synthetically. For further discussion of the origin and synthesis of clay minerals, the reader is referred to
Structure and Properties of Clay Minerals

The following is a brief discussion of the structure and some characteristics of the type of clay of interest in this paper. More complete discussions may be found in textbooks by Grim (16, 17), van Olphen (43), McBain (36) and Brown (10).

The idea that clays were made up of very small crystalline particles is relatively old; however, it was not until the 1920's that the first structural work was done. In 1930 Pauling (38) first described the basic structural units leading to the actual structure of most clays.

The main building elements of most clays are made up of two structural units, a tetrahedral sheet and an octahedral sheet. The tetrahedral sheet is made up of silicon tetrahedrally coordinated to four oxygen atoms. This unit (Figure 1-a) can connect with other similar units by sharing one of its oxygen atoms. These units eventually connect together to form a tetrahedral sheet or more commonly called the silica sheet (Figure 1-b). The second main structural unit, the octahedral sheet, is made up of aluminum or magnesium octahedrally coordinated to six OH groups (Figure 1-c). These units may be put together to form a sheet by the sharing of one face of the octahedron (Figure 1-d). This sheet is commonly called the alumina
Figure 1. Building blocks of clay minerals.
or magnesia sheet, also called the gibbsite layer or brucite layer respectively.

The two sheets or layers just mentioned may be put together to form two main classifications of clays, the two layer minerals and the three layer minerals. The two layer mineral is formed by a bridging of the unshared oxygen of the tetrahedral layer with the octahedral layer by loss of OH groups. The OH groups of the alumina or magnesia layer remain where there are holes in the silica layer due to the hexagonal arrangement of the tetrahedral units. This may be made more clear by noting the overlapping of the two structural units in Figure 2. The three layer minerals are formed in the same way with a tetrahedral layer on both sides of the octahedral layer. The three layer mineral formed with an alumina sheet and two silica sheet is pyrophylite. It is found that the distance between aluminum atoms of different sheets or platelets stacked up (the 001, basal or c-spacing) is about 7.1 to 7.2 Å for two layer minerals and at least 9.2 Å for three layer clays. The length and width of these platelets are in the range of hundreds of angstroms or greater.

The three layer mineral, pyrophylite, just described may be considered the prototype of many three layer minerals. Talc would be the analogous prototype using the magnesia octahedral layer. In the tetrahedral sheet of these materials, tetravalent silicon may be partly replaced by trivalent aluminum. In the octahedral sheet, this
Figure 2. Structural units of clay minerals. (Dotted lines indicate unit cell)
substitution may involve isomorphic replacement with magnesium (in the alumina sheet), iron, chromium, zinc or lithium. Figure 3 shows the structure of pyrophyllite from Hauser (20) and compared to a substituted structure, montmorillonite, after Hofmann, Endell and Wilm (24), Marshall (37) and Hendricks (22). Pyrophyllite, talc, montmorillonite and other related clay minerals belong to the same large group of silicates called montmorillonoids (43).

It may be noted on an examination of Figure 3 that while the charge for a unit of talc or pyrophyllite adds up to zero, the added charge for a unit of the substituted structure gives it a net negative charge. This net negative charge on a platelet of the clay is compensated by cations situated on the surface of the platelet which are too large to penetrate its crystal lattice. Since these cations are on the surface of the clay platelet, they are readily exchangeable. The cation exchange capacity, CEC, is expressed in terms of milliequivalents of exchangeable cation per 100 grams of dry clay. This value ranges from 80 to 150 meq/100g for the montmorillonoids.

Another property of the montmorillonoids is the ability to swell in the presence of water. For this reason, this group is often called the expanding three-layer clays. In vapor phase studies, step-wise hydration has been noted corresponding to one layer and two layers of adsorbed water (9, 25). It is thought that the mechanism of this process involved two processes. First, the hydration of the
Figure 3. Structural units.
cation and second, the adsorption of water on the oxygen surface through hydrogen bonds. The energy released by these two processes is enough to overcome the attractive forces between the platelets and thus expansion occurs. Depending upon the clay and its exchangeable cation, the clay will adsorb up to 0.5g water/g clay. At most its volume may double. When the clay is brought in contact with the liquid, however, the clay platelets may become separated by 100 Å and adsorb up to 10g water/g clay. The clay platelets form a rigid structure analogous to a "house of cards". The result is the formation of a gel.

In the family of montmorillomoids, the one which is of specific interest in this paper is hectorite. Hectorite is a result of the isomorphous substitution of univalent lithium for divalent magnesium in the octahedral (brucite) layer in the talc structure. As in the case of montmorillonite (Figure 3), this substitution results in a net negative charge; therefore, it also has exchangeable cations.

**Organic Complexes of Clays**

Organic complexes of clays may be divided up into two general categories: adsorption complexes and cation exchange complexes. It has been reported (11) that a third type of organoclay complex has been formed in which direct reaction with the clay lattice took place.
There have been no successful attempts to confirm these results, however.

Because of the dipole moment of many organic molecules, it is not surprising to find physical adsorption of these molecules analogous to the adsorption of water. Work has been done (8) to show that interlamellar water is actually displaced by the organic molecule in some cases. This same work postulated from X-ray diffraction data that the polar organic molecule is held to the oxygen surface of the clay through C-H---C bonds from the methylene groups.

As in the case of water, the clay will also form an organic complex by solvolysis of the exchangeable cation. Farmer and Mortland (12) found on adsorption of ethylamine on copper-montmorillonite that the ethylamine solvated the cation with the ethyl group oriented parallel to the silicate surface.

When the clay is placed in the presence of an organic cation such as a quaternary ammonium salt, cation exchange takes place in the same manner as with inorganic ions. The amino groups become strongly attached to the clay surface through the nitrogen. At the same time, the carbon chains attach themselves to the clay surface by way of hydrogen bonding as described previously. This process displaces previously adsorbed water molecules and changes the character of the clay from hydrophilic to the very hydrophobic material (40). Hendricks (21) has shown that the cation exchange capacity
for organic groups is the same as that for inorganic cations except for very large organic cations which tend to overlap exchange sites. Slabaugh (40) calculated the equilibrium constants involved with the reaction:

$$\text{Na}^- \text{Bentonite} + \text{RNH}_3^+ \rightleftharpoons \text{Na}^+ + \text{RNH}_3^- \text{Bentonite}.$$ 

The equilibrium constants varied from 0.77 for methylamine and increased with increasing chain length to 102 for octadecylamine ions.

The organoclay complexes formed by cation exchange have an ability to form gels with organic solvents in a manner analogous to the clay-water system previously mentioned. Jordan (27, 28, 30, 31) has studied this property in detail. He has determined that gelation is slight in a nonpolar organic liquid and increases, in general, with increasing dielectric constant of the liquid. The best gelation occurred with a liquid which combines both polar and nonpolar characteristics such as nitrobenzene or a binary mixture such as 3% ethanol in heptane. He concluded that the gelation process involved the high adsorption energy of the polar groups on the silicate surface forcing the platelets apart. The carbon chains of the amine groups are then exposed to be solvated by the bulk liquid. Hiltner (23) found that c-spacings of the platelets increased by about the length of the amine carbon chain on adsorption of a polar organic molecule. Heptane adsorption did not expand the clay platelets but it was adsorbed to a very great extent when a polar component had been preadsorbed.
This then tends to support Jordans conclusions.

**Selective Adsorption from Binary Solution**

Although much work has been done in the past on adsorption of vapors on solid surfaces, relatively little has been done on the adsorption from the liquid phase.

Beginning in the 1920's a few workers had begun to measure the adsorption of components A and B from a binary mixture by determining the change in concentration of that mixture. The usual type of isotherm obtained, plotting change in concentration versus concentration of the mixture, is an "S" shaped curve centered around the horizontal ordinate (concentration of solution before adsorption). The data usually shows a positive adsorption of the component A at low concentration. As the concentration of component A increased, the curve will cross the axis to give seemingly negative adsorption of component A. The true interpretation of these isotherms, however, is in terms of a comparison between the concentration of the bulk solution to the concentration of the solution adsorbed on the solid surface. Positive adsorption of the component means the adsorbed phase is richer in that component than the bulk liquid and vice versa. It can therefore be seen that if a surface adsorbed the solute and solvent molecules in a definite ratio, the isotherm described should go from "positive adsorption" to "negative adsorption" of component A. The
mole fraction where the adsorption changes from "positive to negative" can be said to be equal to the ratio of the molecules adsorbed at the solid liquid interface. The misleading terms, positive and negative adsorption, were rejected by Bartell and Sloan (5) for the more preferred terms, preferential or selective adsorption. Another type of isotherm which is sometimes obtained is a "U" shaped curve in either the positive or negative direction, indicating the preferential adsorption of one component.

One of the first studies made on adsorption from binary solution was made by Bartell and Sloan (5, 6) in 1929. They described the selectivity factor in terms of adhesion tension of the liquids to the adsorbent, this being analogous to the interfacial tension in Gibbs principle. An equation was derived to describe the preferential adsorption over the entire concentration range assuming that the adsorption of each component followed the Freundich equation. Following this work, Bartell and co-workers (2, 3, 4) made several studies on the adsorption of organic liquid mixtures on carbon and silica. The results of this work was interpreted qualitatively in terms of properties of the adsorbent (organophilic verses hydrophilic properties). It was indicated that the degree of adsorption of one component is dependent upon the adhesion tension of that component compared to the adhesion tension of the solvent. In the case where adhesion tensions are similar for a series of compounds, the degree
of adsorption is governed by the solubility of the adsorbate: the
greater the solubility, the less the tendency to be adsorbed.

Kane and Jatkar (32) also made note of the properties of the
binary mixture in relation to the selectivity of adsorption. They pro-
posed the existence of stoichiometric "complexes" of acetic acid and
toluene adsorbed on the surface of charcoal, thus giving a constant
concentration in the adsorbed phase. Komarov and Etmolenko (34,
35) have also proposed that the selective nature of adsorption from
binary solution is related to the nature of the binary mixture and not
the adsorbent.

Selective adsorption from the vapor phase also shows the famil-
liar "S" shaped isotherms found in adsorption from the liquid phase.
Tryhorn and Wyatt (41, 42) studied the adsorption of alcohol and
benzene, and acetone and benzene vapor mixtures on charcoal. They
interpreted the isotherms in terms of three different stages of ad-
sorption: first, adsorption of the vapor at constant ratio; second,
condensation of the mixture; and third, adjustment of the condensed
liquid so as to be in equilibrium with the bulk liquid. This may be
one explanation for vapor phase adsorption but it cannot explain the
same type of isotherms from liquid phase adsorption.

Isotherms for selective adsorption from vapor phase have been
found to agree quite well with adsorption isotherms from liquid phase
(26, 33). Kipling and Tester (33), studying both the liquid and vapor
phase adsorption, have found that neither the Freundlich equation (as proposed by Bartell and Sloan) nor the Langmuir equation are adequate to describe the adsorption isotherms they observed. They proposed an equation which fit their experimental data very well based on the assumption that the adsorbent is covered at all times by a unimolecular layer of adsorbate. This treatment has been used successfully by Kipling and co-workers (7, 13) to describe the adsorption of many different binary mixtures on silica and charcoals. Hansen and Hansen (19), however, criticized the treatment of adsorption proposed by Kipling and Tester. They proposed a pore-filling mechanism which, although a different theoretical approach, gives essentially the same theoretical isotherms as Kipling.

Although vapor or gas adsorption is a more common means of surface area determination, adsorption from binary solution has also been studied for this purpose (15, 26). This method, although experimentally simple, is much more complicated theoretically. One must take into account the fact that two different molecules are being adsorbed instead of just one. There is also the problem of determining the size and orientation of the adsorbate. Hansen, Fu and Bartell (18) and Bartell and Donahue (1) have proposed that adsorption from solution is multimolecular and follows the B. E. T. equation for the case of adsorption of slightly soluble organic compounds from aqueous solution. Surface areas of charcoals, graphites, carbon blacks and
silica gel were determined by this method. Giles, MacEwan, Nakhwa and Smith (14) have furthered this work by the classification of isotherms for adsorption from solution analogous to the B.E.T. classification of isotherms in gas phase.
EXPERIMENTAL

Apparatus

The changes in concentrations caused by selective adsorption were determined by refractive index changes of the binary solution. This procedure has been reported by other investigators (13, 32, 33) using a Pulfrich refractometer to determine selective adsorption on charcoals and silica gel. The method selected for this study does not measure the refractive index directly but measures the difference in refractive index of the solution added to the clay compared to the same solution not added to the clay. This measurement is made by a differential refractometer.

The differential refractometer was selected in place of a normal refractometer for two reasons. First, the differential refractometer is able to compare two samples directly and thus receive the concentration difference on a single reading. The differential refractometer also has greater precision. Refractive index differences may be measured to six decimal places with less effect due to temperature changes, whereas a normal refractometer would under similar conditions measure to only four decimal places. Readings were made by thermostating to $\pm 0.1^\circ$C.

The instrument used was a Brice-Phoenix Model BP-2000-V differential refractometer. A Mercury Vapor Lamp, type AH-3, was
used as the light source which passed through a blue filter to isolate the 436 μm wavelength. The differential refractometer cell was made of optically polished glass measuring 1.5 centimeters by 1.5 centimeters (inside dimensions). The partition between the two halves of the cell is such as to form an angle of incidence of 69° with the normal to the surface of the partition. This cell is good for refractive index liquids up to 1.62. To prevent evaporation while taking a reading, the cell was modified by cementing a brass plate on the top with epoxy cement. It could be removed easily by warming for cleaning the cell. Two capillary tubes per cell section were soldered onto the brass plate to add and remove samples from each half of the cell individually. This whole cell assembly was thermostated with a water jacket at 25.0 ± 0.1°C. The change in light path due to difference in refractive index was detected by a microscope with traveling cross hair. The instrument was calibrated in hundredths of millimeters, where 0.01 mm = 0.000018 refractive index difference.

Clay Materials and Reagents

The organoclay used in this investigation was one of the organo-clay complexes produced by the Baroid Sales Division of the National Lead Company. It is sold under the trade name of Bentone-38. This is the dimethyldioctadecylammonium salt of hectorite. In the
production of this organoclay, a 25% excess of the quaternary ammonium ion is added to the clay. It was therefore necessary to extract the excess quaternary amine in a Soxhlet extractor with isopropyl alcohol for 48 hours. The extracted clay was then placed in a vacuum oven at 40-50°C for 12 hours and hand-ground to 120 mesh. A sample of sodium hectorite, also from Baroid, was used with no preparation for a comparison with and without the amine.

A single hydrocarbon, toluene, was used along with a series of polar solvents to make up the binary solutions. The polar solvents used were methanol, ethanol, n-propanol, isopropanol, n-butanol, acetone, 2-butanone and nitromethane. All the solvents were of reagent grade except nitromethane which was distilled at 100.5°C to 101.0°C.

Procedure

One of the most serious problems faced in determining the analytical procedure was the change in concentration of the binary solutions due to evaporation or to absorption of water vapor from the air. It was therefore decided that all the samples should be sealed in glass ampoules. For the solution that was to be in contact with the clay, 14 millimeter pyrex tubing was made into test tubes about 150 millimeters long. Glass beads were placed in the tubes to help in mixing and the ends were drawn out to facilitate sealing off the tube
once filled with the sample. The resulting tube would hold ten milliliters of solution plus the clay sample. Even though only 1-1.5 milliliters were needed for analysis, ten milliliter samples were used so that at maximum gelation there would be sufficient supernatant liquid to analyze. Smaller tubes of ten millimeter pyrex tubing were made up in the same manner to hold the standard solution which was not added to the clay. These smaller tubes held three milliliters. It was found that water vapor absorption and condensation occurred while making the sample tubes. All the tubes were therefore dried in an oven and stored over calcium chloride until used.

Clay samples of 400 milligrams were weighed out to within 0.1 milligram and placed in the 14 millimeter tubes. This amount was the maximum sample which could be used and still get enough supernatant liquid to analyze at maximum gelation. The binary solutions were made up in 50 milliliter aliquots by volume-volume percent which were recalculated in terms of mole fraction. Ten milliliter portions of the aliquot were added to each of three clay samples. The tubes were then sealed with a torch while keeping the liquid sample under acetone-dry ice. This was to reduce evaporation while sealing the tubes. Standards were also sealed in the small tubes at the same time.

The sealed samples were then shaken for at least an hour to
disperse the clay throughout the solution. In some cases, where maximum gelation occurred, it was necessary to put the tubes on a vibrator to break up large aggregates of clay. The samples were then placed in a thermostated air bath at $30^\circ \pm 0.1^\circ$ C to come to equilibrium for at least 12 hours. An attempt was made to determine the length of time to come to equilibrium; however, uniform mixing could not be achieved for all samples. There is evidence (39) that the adsorption process takes place over a period of just a few minutes. The samples probably came to equilibrium while mixing and the 12 hours was used to reequilibrate to the temperature at $30^\circ$ C.

It was found that adsorption on the refractometer cell walls took place with any sample placed in it. Consequently, the walls desorbed into the next sample. This desorption would tend to change the concentration of the solution within the cell by about 0.001 to 0.005 mole fraction, which is about the concentration changes due to selective adsorption. It was therefore found necessary to rinse the cell with a solution of concentration nearly equal to that of the solutions being compared. The procedure was to rinse out both halves of the cell with one of the scaled standards. This solution was then removed from the cell by an aspirator. A second standard was then placed in both halves of the cell, and the capillary tubes were plugged to prevent evaporation. A zero reading was then taken. This zero reading was necessary because the construction of the instrument did
not give the same zero reading with different standards. The solution from half the cell was then removed, leaving the other half sealed with the standard. About 1.5 milliliters of the supernatant liquid from the clay suspension was drawn off and placed into this half of the cell. This suspension had been previously centrifuged for ten minutes at 1000 revolutions per minute. A final reading was then taken. The difference between the zero reading and the final reading was thus related to the concentration change. For each concentration, three readings were taken for three different samples.

The instrument was calibrated such that the difference in zero reading and final reading, in millimeters, could be directly related to the concentration difference. A calibration constant (in units of millimeters per percent concentration difference) was determined using the same procedure as previously described substituting another known standard of different concentration for the sample mixture.
EXPERIMENTAL RESULTS AND DISCUSSION

Selective adsorption of the series of polar solvent-toluene mixtures by B-38 are shown in Figures 4-12. Table 1 gives a summary of the properties of the systems studied. The isotherms are plotted on the usual coordinates, \( n (\Delta x/m) \) verses \( x \), where \( x \) is the mole fraction of the bulk solution before adsorption, \( \Delta x \) is the change in mole fraction of the polar component in the bulk solution due to selective adsorption and \( n \) is the total number of millimoles in contact with \( m \) grams of clay. A positive value of \( n (\Delta x/m) \) indicates preferential adsorption of the polar component or that the adsorbed phase is richer in polar component than the bulk solution. A negative value indicates preferential adsorption of toluene.

In considering the series of alcohols, it may be noted (Table 1) that the composition of the adsorbed phase (given by the crossing point) increases in the order,

\[
\text{Methanol} > \text{Ethanol} > \text{Isopropanol} \simeq \text{n-Propanol} > \text{n-Butanol}
\]

This arrangement may seem unexpected considering the organophilic nature of the clay. However, if the polar group adsorbs on the oxygen layer of the clay platelet, it is not so surprising that methanol will adsorb to the greatest extent.

Two reasons may be noted for the order of adsorption of the series of alcohols. First, the polarity is generally decreasing and
Table 1. Properties of polar adsorbates in a toluene solution.

<table>
<thead>
<tr>
<th>Polar Component</th>
<th>Composition of Adsorbed Phase at Crossing Point</th>
<th>Dielectric Constant of Polar Component</th>
<th>Azeotropic Composition with Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>44.3%</td>
<td>32.6 @ 25°</td>
<td>72.4%</td>
</tr>
<tr>
<td>Ethanol</td>
<td>42.7%</td>
<td>24.3 @ 25°</td>
<td>68.0%</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>32.0%</td>
<td>20.1 @ 25°</td>
<td>49.0%</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>34.0%</td>
<td>18.3 @ 25°</td>
<td>58.0%</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>24.5%</td>
<td>17.1 @ 25°</td>
<td>27.0%</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>58.0%</td>
<td>39.4 @ 20°</td>
<td>55.0%</td>
</tr>
<tr>
<td>Acetone</td>
<td>100.0%</td>
<td>20.7 @ 25°</td>
<td>---</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone</td>
<td>65.0%</td>
<td>18.7 @ 20°</td>
<td>---</td>
</tr>
</tbody>
</table>
Figure 4. Adsorption of Methanol-Toluene on B-38.
Figure 5. Adsorption of Ethanol-Toluene on B-38.
Figure 6. Adsorption of 2-Propanol-Toluene on B-38.
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Figure 8. Adsorption of n-Butanol-Toluene on B-38.
Figure 9. Adsorption of Nitromethane-Toluene on B-38.
Figure 10. Adsorption of Acetone-Toluene on B-38.
Figure 11. Adsorption of Methylethylketone-Toluene on B-38.
Figure 12. Adsorption of Methanol-Toluene.
the organic character increasing with increasing carbon chain length. The adsorption of methanol and toluene on sodium- Hectorite (Figure 12) shows that the hydrocarbon is not selectively adsorbed on the clay surface. It may be seen, therefore, that as the solvent's polarity decreases and its organic character increases, the solvent molecules will be adsorbed to a lesser extent. The second reason for this order is that the increasing size of the solvent molecule allows fewer molecules to be adsorbed. If the factor of size is the main consideration, it would indicate that the adsorbate molecules are lying horizontal to the plane of the platelet rather than vertical. This type of adsorption has been reported previously by Bradley (8).

It may be noted from Table 1 that nitromethane is adsorbed to a greater extent than methanol although it is a slightly larger molecule. Hiltner (23) has reported, however, that gas phase adsorption and x-ray studies have led her to believe that the nitromethane molecule is partially sunk into the oxygen surface. The result is a smaller effective molecule. It must be considered, therefore, that nitromethane is consistent with both stated causes for the order of adsorption.

Jordan and co-workers (30) studying the gelation of organoclay complexes in alcohol-toluene systems have reported the order of gel strength to decrease in the same manner as the concentration of the the adsorbed phase decreases. This reemphasizes the conclusions of
Jordan, that the concentration of the polar component on the clay surface is critical in the formation of a gel structure. This point is again stressed on noting that in the concentration range where maximum gel strength is observed (between 0 and 0.1 mole fraction), the adsorbed phase is richer in polar component in every case. Apparently, the adsorbed liquid which is needed to form the gel structure is a relatively small amount compared to the total liquid integrated into the structure.

The discussion thus far has been confined strictly to the properties of the polar component and the properties of the organoclay complex. The ideas put forth do not, however, explain the behavior of acetone, methylethylketone and isopropanol. Acetone and methylethylketone have dielectric constants comparable with n-propanol and isopropanol respectively and sizes comparable with isopropanol and n-butanol respectively. The adsorption of the two ketones, however, is quite different from that shown by the isotherms of their alcohol counterparts. The observation that the composition of isopropanol in the adsorbed phase is slightly greater than n-propanol is also just reversed from dielectric constant considerations.

The relative gel strengths of the polar dispersing agents used are in the order (29, 30).

Nitromethane > Acetone > methylethylketone > Methanol > Ethanol > Isopropanol > n-Propanol > n-Butanol
In order to explain this order of decreasing gelling ability and to correlate the selective adsorption of these components, a third property of the system was examined, namely, the interaction between the polar component and the hydrocarbon. It is proposed that if the polar component is associated with the hydrocarbon in a certain ratio such as in the case of an azeotropic mixture, the polar molecule will tend to pull the hydrocarbon molecules along with it as it adsorbs onto the clay surface. The hydrocarbon molecules which are pulled along with the polar molecules will tend to hinder further adsorption and reduce the number of adsorbed molecules.

Referring to Table 1, it may be noted that on the basis of azeotropic mixture influencing the composition of the adsorbed phase, the position of isopropanol in the concentration series may be explained. The adsorption of the two ketones is also more fully understood. Since neither acetone nor methylethylketone form azeotropes with toluene, the ketone molecules would be hindered less when they adsorb on the clay surface. As Figures 10 and 11 show, toluene is selectively adsorbed to only a small extent if at all from the toluene-ketone mixtures. It is also noted that both ketones produce better gels than the alcohols. It should be kept in mind that the hydrocarbon molecules only hinder further adsorption. Even though nitromethane forms an azeotrope of composition comparable to isopropanol, its small size and high dielectric constant make it a better adsorbate.
The overall picture proposed for the gel structure of an organo-clay is one in which the adsorbed polar component plays a very important part. Since the silicate surface of the clay is hydrophilic, a polar organic molecule is first needed to get between the clay platelets and pry them apart. The clay platelets expand to form a "house of cards" structure. This structure may be thought of as composed of cells or "rooms" with the clay platelets serving as the walls of the cells. These cells are probably interconnected because of the irregular shapes of the clay platelets; however, they may be thought of as definite structures which hold a portion of the hydrocarbon molecules. The cells are held together by the solvation by the hydrocarbon component of the cell walls and the hydrocarbon chain from the amine. The amine hydrocarbon chain may be thought of as extending away from the clay surface towards the interior of the cell. This would have a stabilizing effect to the structure in a manner analogous to the stabilization of a plant by the extension of its roots into the ground.

If the theory is accepted that the gel structure is made up of a continuous array of cells analogous to the "house of cards" and held together by the solvation of the hydrocarbon, the gel strength must be directly proportional to the solvation energy. For any given amine and hydrocarbon, the strength of the gel structure will depend upon the ability of the hydrocarbon to solvate the walls of the cells. As pointed out previously, the hydrocarbon has little tendency to solvate
the silicate surface. The second need for a polar organic component in the binary mixture, therefore, is to adsorb onto the silicate surface, thus changing the clay surface from hydrophilic to organophilic. The more efficiently the packing of the polar molecules on the silicate surface, the more organophilic the surface becomes; therefore, the better it is solvated by the hydrocarbon.

It may be seen from the preceding discussion that the more a polar component is adsorbed onto the silicate surface, the stronger the gel structure. The best gelling agent is therefore going to be a polar organic molecule which can adsorb strongly onto the silicate surface. Only a small percentage of this component is needed, or enough to cover the silicate surface. Hiltner (23) found this amount to be less than 100 mg/g clay in all cases. The selective adsorption of the hydrocarbon component of the binary system may do little or nothing to strengthen the gel structure and may actually tend to weaken it.
SUMMARY AND SUGGESTIONS FOR FURTHER WORK

It has been found that to form a gel with an organoclay complex, an organic solvent along with a polar solvent must be used. For this reason, a study of the adsorption selectivity from a polar-nonpolar solvent system might be of interest in the study of the gel structure.

Adsorption from binary solution was determined by measuring the change in concentration due to selective adsorption by the dimethyldioctadecylammonium salt of hectorite. This change in concentration was then plotted verses concentration which gave an "S" or "U" shaped isotherm, depending upon the polar adsorbate. The point at which no concentration change was observed was assumed to be the concentration of the adsorbed phase.

The relative ability for the polar component to adsorb onto the organoclay complex was correlated with three properties of this component: size, dielectric constant and interaction with the hydrocarbon component. This adsorption ability was, in turn, related to the gel strength. A model of the gel structure was proposed based on the ability of the polar component to adsorb onto the silicate surface of the clay and the hydrocarbon to solvate the resulting organic surface and amine cations.

Several suggestion may be made for further work in connection with this study.
1. An extension of the study might be made to include a larger series of alcohols and ketones. Other polar adsorbates might also be investigated such as ethers, halogenated compounds or nitriles.

2. Since the formation of azeotropes has been considered a factor for gelation, a study of a single polar component with different hydrocarbons which form a series of azeotropic compositions might be of interest.

3. It has been noted that organoclay complexes with amine chains with less than 12 carbon atoms have little organophilic properties. A study of selective adsorption on these organoclays might be of interest when compared to this study.
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