

ROLE OF EXCHANGEABLE CATIONS IN VISCOSITY OF CLAY SUSPENSIONS

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ABSTRACT

A study was made of the changes in viscosity of Wyoming bentonite suspensions with variations in cation ionization, base saturation, clay concentration, sodium chloride concentration and type of exchangeable cation. There is little change in the viscosity with decreasing cation ionization until a certain threshold value is reached. Below this value the viscosity increases rapidly, indicating that the repulsive potential barrier has been reduced to the order of the kinetic energy of the particles. Unfortunately, a quantitative estimate of the ionization was not possible at this value because of the high salt content of the system.

Exchangeable aluminum was found to act as a strong bonding agent between clay particles in the pH range 4.50–5.50. This was explained on the basis of the formation of multivalent, aluminum-hydroxyl complex ions.

INTRODUCTION

The interaction of clay particles in an aqueous medium is of interest from a colloid chemistry standpoint as well as in the technical fields of drilling mud technology, soil physics and clay sedimentation. Recently, two mechanisms have been proposed to explain the association of clays in dilute salt-free suspensions. Van Olphen (1956) considers the interaction to be between the positive edges of one particle and the negative surfaces of another. However, M'Ewen and Pratt (1957), and M'Ewen and Mould (1957) have concluded from optical measurements that there is an edge-to-edge association of particles forming flat ribbons. The work presented here is consistent with either of these views since the measurements reveal only the gross result of a particle-to-particle association. In order to explain the gelation properties of these suspensions it is necessary to assume that association can occur between particles at certain points on their surface but not at others. If association could occur between any points on the surface, complete flocculation would result. Conversely, if no association occurred, the particles would remain in a suspended state. In order to form an interlacing network of particles throughout the dispersion medium it is necessary that the particles be in a state intermediate between dispersion and flocculation. This dual nature of the clay particles may be due to a difference in the charge distribution of the exchangeable ions at the edges compared to the planar surfaces resulting in different repulsive potentials. Alternately, it may be explained by assuming that part of the surface is hydrophilic and part hydrophobic. This latter approach has been used in this paper. These terms, as used here, refer to the

sensitivity of the clay surfaces to flocculation by electrolytes. In this meaning of the two terms there is no difference in the two explanations. One may think of a surface with a high repulsive potential as having exchangeable ions that are extended a considerable distance into the dispersion medium. Therefore, the dispersion medium in the double layer, for practical purposes, is associated with the particle surface and the surface would be hydrophilic, according to the classical definition of the term. A hydrophilic surface is equivalent to a high repulsive potential, and a hydrophobic surface is equivalent to a low repulsive potential.

The objective of this study was to determine, through the measurement of viscosity, the interaction of montmorillonite clay particles under conditions of varied cation ionization, base saturation, clay concentration, sodium chloride concentration and type of exchangeable cation.

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EXPERIMENTAL PROCEDURE

Wyoming bentonite obtained from the Baroid Sales Division of the National Lead Company was used throughout this research. The natural clay was suspended in distilled water and the fraction to be studied ($<0.3 \mu$) was separated with the International no. 2 centrifuge. It was then converted to the hydrogen form by passing through columns of hydrogen- and hydroxyl-saturated exchange resins (Illco C-211 and Illco A-244, respectively).

Hydrogen-sodium systems and hydrogen-calcium systems were prepared by titrating the hydrogen clay with freshly prepared sodium or calcium hydroxide. The aluminum-saturated clay was prepared by leaching with 1 N AlCl_3 and removing the excess salt by washing with distilled water until no chloride was detected in the leachate. Hydrogen-aluminum systems and sodium-calcium systems were prepared by mixing the homoionic clays in the desired proportion. Suspensions containing sodium chloride were prepared by adding solutions of the salt to clay suspensions of known concentration and cation saturation.

Measurements of the pH were made with the Beckman H2 glass electrode pH-meter. Sodium activities were determined by the clay membrane method of Marshall (Marshall and Bergman, 1942). Conductivity measurements were made with a dip cell using a Leeds and Northrup 60 c/s a.c. galvanometer and Wheatstone bridge. The viscosity was determined with an Ostwald viscometer.

RESULTS

Sodium-hydrogen Clay Suspensions

Titration with sodium hydroxide.—The change in the ionization of sodium with addition of NaOH to the hydrogen clay suspension (0.773 percent) is shown in Fig. 1, along with the corresponding viscosity changes. The most obvious feature of the activity curve is the sharp increase in sodium activity at the equivalence point along with the corresponding decrease in cationic bonding energy.¹ Accompanying this change in activity there is a decrease

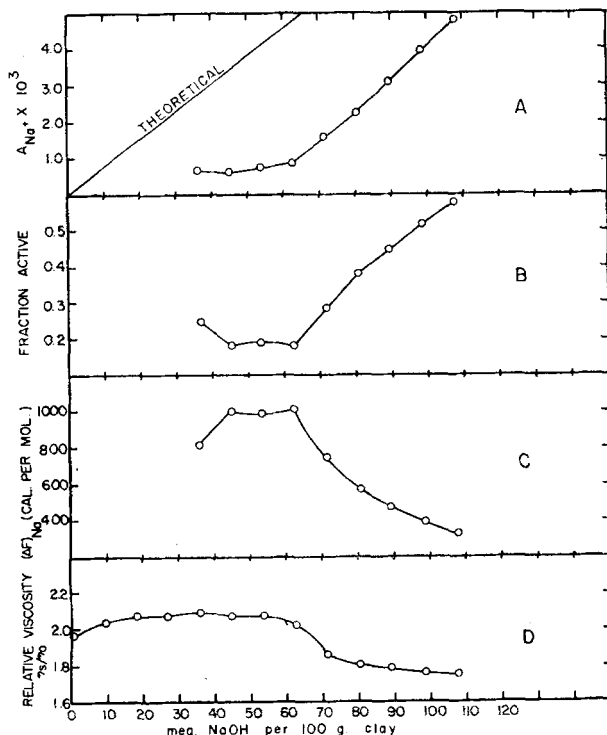


FIGURE 1.—Clay titration curve for 0.773 percent Wyoming bentonite (fraction $< 0.3 \mu$) with sodium hydroxide. *A*: sodium ion activity (moles/l.). *B*: fraction active. *C*: mean free bonding energy of sodium. *D*: relative viscosity of clay suspension.

in viscosity. At first glance, this might be taken as proof that an increase in ionization results in a decrease in the association between particles with a corresponding decrease in viscosity. However, it must be remembered that this change occurs after the equivalence point and does not represent ionization of the surface. It merely represents an addition of sodium hydroxide

¹ Using the terminology of Marshall (1950) the cationic mean free bonding (ΔF)_{cation} is defined as $(\Delta F)_{\text{cation}} = RT \ln c/a$ where c is the total concentration of the cation and a is the measured activity. The fraction active, f , is defined as a/c and is a measure of the degree of ionization.

to the external solutions. In fact, we might expect this addition of excess electrolyte to depress the ionization of the adsorbed cations. The fact that the activity measurements do not indicate a depression of ionization and that the viscosity decreases constitutes an apparently anomalous reaction. Perhaps the most obvious explanation would be that hydroxyl ions are adsorbed to the clay surface, thereby increasing the exchange capacity of the clay and providing a greater density of surface charge. However, the adsorption of hydroxyl ions seems to be minor, because both the sodium

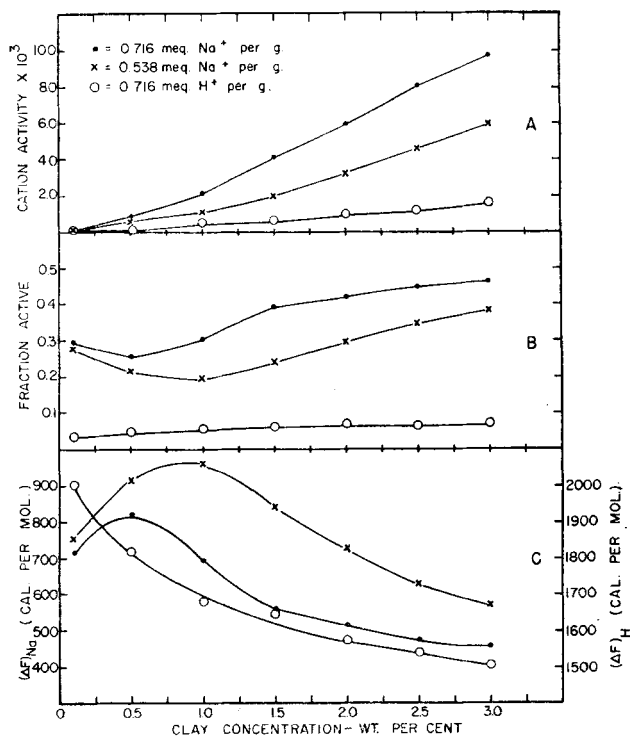


FIGURE 2.—The effect of clay concentration on the ionization of Wyoming bentonite (fraction $< 0.3 \mu$). *A*: sodium and hydrogen ion activities (moles/l.). *B*: fraction active. *C*: cationic mean free bonding energy.

activity and the conductivity increase linearly and at about the same rate as for sodium hydroxide alone. An alternate hypothesis is that exchangeable aluminum, which significantly affects the viscosity, becomes ineffective at this point. This possibility will be considered in more detail later.

Effect of clay concentration on viscosity.—Changes in viscosity and cation activity with increasing clay concentrations have been determined for three levels of base saturation—approximately 100 percent hydrogen, 75 percent sodium, and 100 percent sodium. The cation activity data are presented in Fig. 2, which shows a steady increase in cation activity and a decrease in

cationic bonding energy with increasing clay concentration. The low bonding energy for the dilute clay suspensions containing exchangeable sodium is probably due to Donnan hydrolysis. Note that with an increase in clay concentration the degree of ionization (fraction active) increases. This is in contrast to the behavior predictable by the interionic attraction theory of strong electrolytes. This effect was also substantiated by conductivity measurements.

If particle association is directly proportional to clay ionization, a decrease in reduced viscosity with increased clay concentration is to be expected. The viscosity curves in Fig. 3 indicate, however, that there is a definite *enhancement* in viscosity with increased clay concentration. The viscosity in Fig. 3 is expressed as reduced viscosity (viscosity per unit volume of clay), thereby

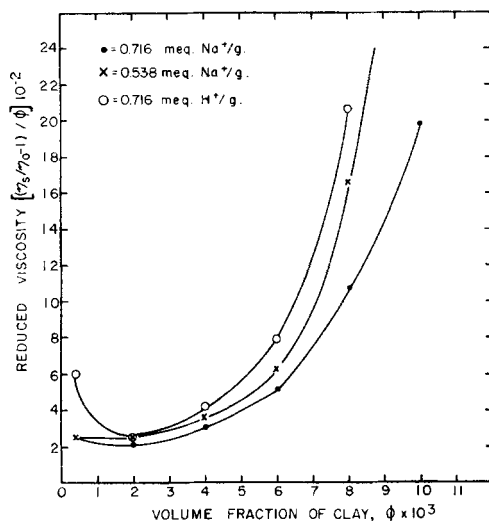


FIGURE 3.—Variation of reduced viscosity $\left[\frac{\eta^s}{\eta^0} - 1/\phi \right]^*$ with concentration of Wyoming bentonite (fraction $< 0.3 \mu$) for cation saturations of approximately (1) 100 percent sodium, (2) 75 percent sodium—25 percent hydrogen, and (3) 100 percent hydrogen.

accounting for the expected change due to increased concentration of clay. The sharp increase in viscosity at the high clay concentrations is probably due to the interference between particles resulting in a greater resistance to orientation.

Some indication of the effect of cation ionization on the viscosity of clay suspensions can be obtained from curves 1 and 3 of Fig. 3. The viscosity of the hydrogen-saturated clay (no. 3) is consistently greater than that of the sodium-saturated clay. Along with this higher viscosity of the H-saturated clay, there is a much smaller cation activity and fraction active (ionization). The difference in viscosity, however, is not as great as one might expect

* ϕ refers to volume fraction of clay in suspension.

from comparison of the fractions active of the two systems. A sixfold decrease in fraction active results in only a twofold increase in viscosity, indicating that factors other than ionization are involved in the interaction of particles.

Effect of sodium chloride on viscosity.—The curves of Fig. 4 show the change in viscosity with increasing sodium chloride concentration for two levels of sodium saturation. From consideration of the effect of electrolytes on the ionic double layer, one would expect the addition of sodium chloride to enhance the association of clay particles and thereby increase the viscosity of the suspension. The data show that this holds only at high concentrations of sodium chloride. In fact, the first additions of sodium chloride cause a decrease in viscosity. This effect may be due to the adsorption of chloride on the clay. Measurement of the chloride activity with an Ag : AgCl electrode indicates that there is indeed some adsorption of chloride ions. Sodium ion

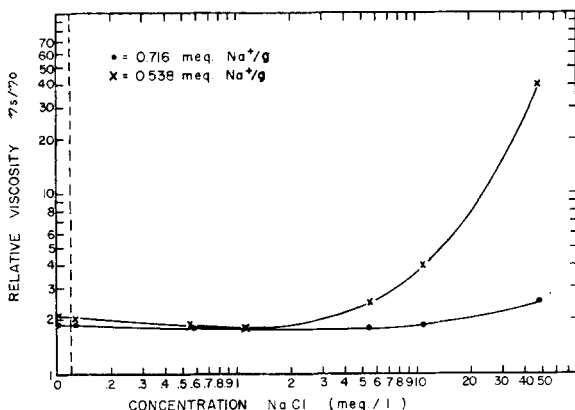


FIGURE 4.—Variation of relative viscosity of Wyoming bentonite suspensions (concentration 0.773 percent, fraction $< 0.3\mu$) with sodium chloride concentration for sodium saturations of approximately (1) 100 percent and (2) 75 percent.

activity measurements on the same material show that the amount of non-ionized sodium is constant up to about 0.01 N NaCl. Hence the sodium associated with the adsorbed chloride is in a completely ionized state, thereby increasing the amount of sodium in the double layer.

The viscosity of the two clay suspensions at various sodium saturations differs at the high concentrations of sodium chloride. This is true even though the sodium activity, chloride activity, and conductivity are similar. This difference may be due to the presence of adsorbed aluminum. As we shall see later, the presence of aluminum significantly affects the interaction of clay particles.

The effect of sodium chloride on viscosity for various degrees of base saturation is shown in Fig. 5 (calcium) and Fig. 6 (sodium). The most significant feature of these curves is the maximum which occurs at a base content of about 50 meq/100 g and in the pH range, 4.50–5.50. This maximum is common to both the sodium–hydrogen and the calcium–hydrogen systems

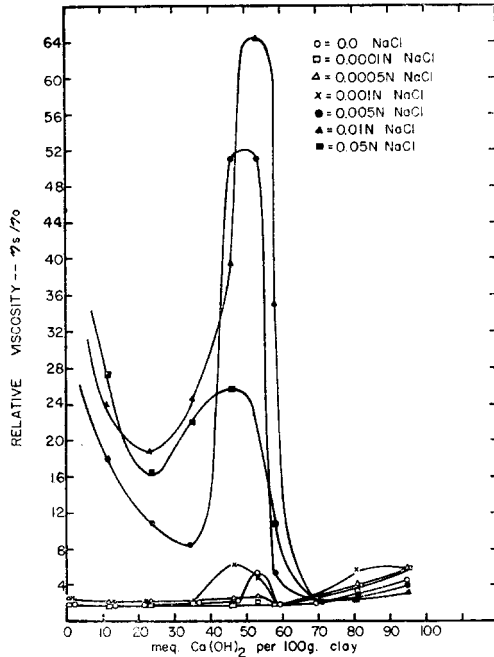


FIGURE 5.—Variation of relative viscosity of Wyoming bentonite suspensions (concentration 0.663 percent, fraction $<0.3\mu$) with increasing calcium saturation and sodium chloride concentration.

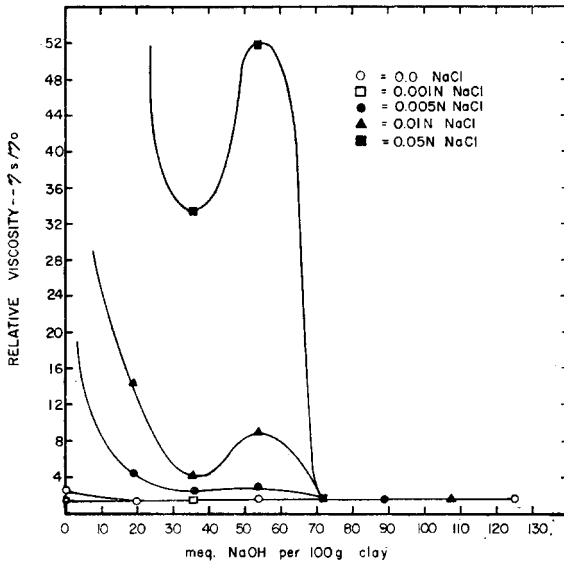


FIGURE 6.—Variation of relative viscosity of Wyoming bentonite suspensions (concentration 0.663 percent, fraction $<0.3\mu$) with increasing sodium saturation and sodium chloride concentration. Note: on this scale NaCl concentrations 0.0001, 0.0005, and 0.001 fall on the same curve.

and corresponds to 75 percent base saturation. These maxima probably are due to exchangeable aluminum on the clay. The clays were in the hydrogen-saturated form for 30 days prior to use—sufficient time for an appreciable quantity of aluminum to be released from the crystal lattice of the clay.

Effect of exchangeable aluminum on viscosity.—The change in the viscosity of the clay suspension as the Al : H ratio on the exchange complex increases is shown in Fig. 7. As the aluminum content increases the viscosity increases to a maximum at about 50 percent aluminum saturation. Further increases in aluminum saturation result in a decrease in viscosity. This increase in

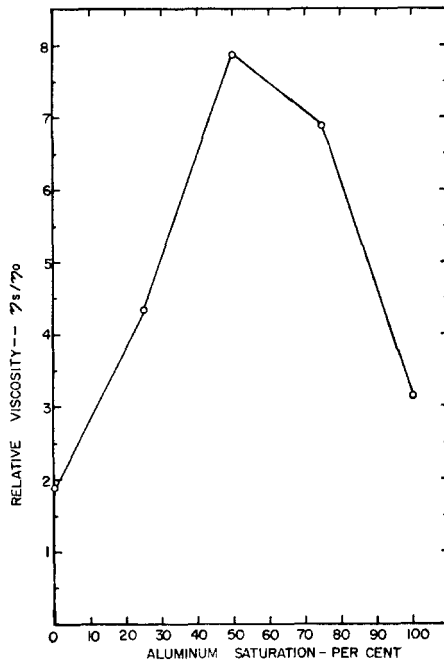


FIGURE 7.—Variation of relative viscosity of a suspension of Wyoming bentonite (concentration 0.778 percent, fraction $<0.3\mu$) with replacement of exchangeable hydrogen by aluminum.

aluminum content is accompanied by an obvious increase in the size of the flocs formed. Apparently there is an optimum degree of flocculation for maximum viscosity.

The titration of the hydrogen-aluminum clays with sodium hydroxide results in a decided change in the suspension viscosity (Fig. 8). In all cases the first addition of sodium hydroxide causes dispersion of the clay with the corresponding decrease in viscosity. Further additions of sodium hydroxide show only a minor effect, with some indication of a maximum.

In Fig. 9 the viscosity curves are presented for the titration of freshly prepared hydrogen-saturated clays with sodium hydroxide. The change in

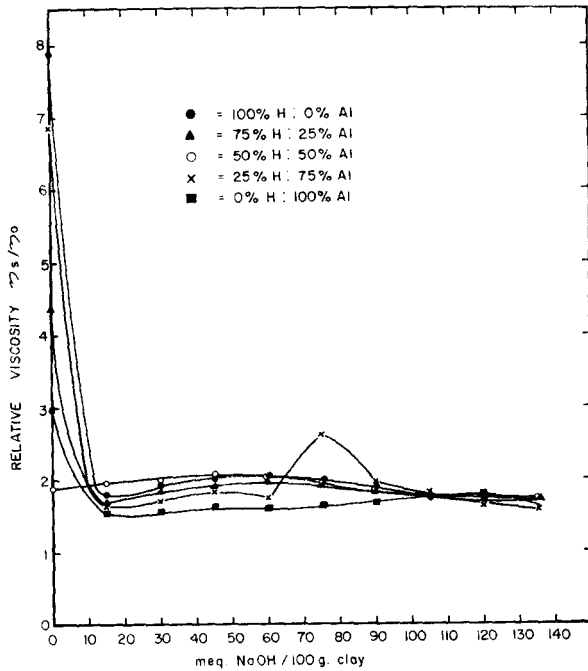


FIGURE 8.—The relative viscosity of Wyoming bentonite suspensions (concentration 0.778 percent, fraction $<0.3\mu$) titrated with NaOH at five H : Al ratios.

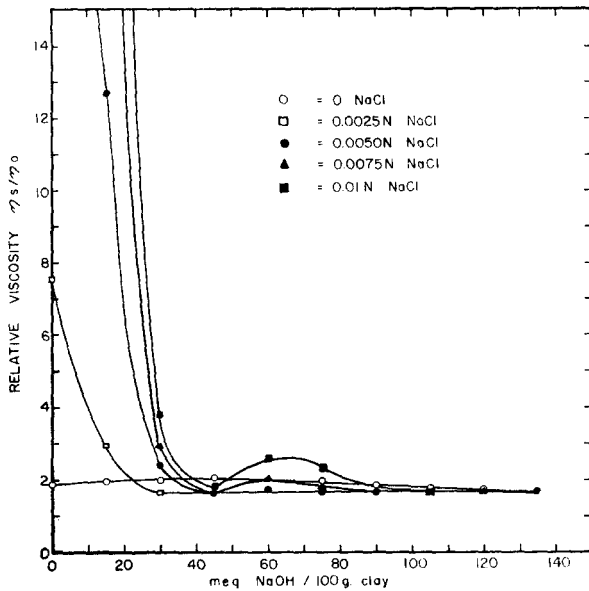


FIGURE 9.—Variation of relative viscosity of Wyoming bentonite suspensions (concentration 0.778 percent, fraction $<0.3\mu$) with increasing sodium saturation and sodium chloride concentration. The clay, prior to titration, was hydrogen saturated.

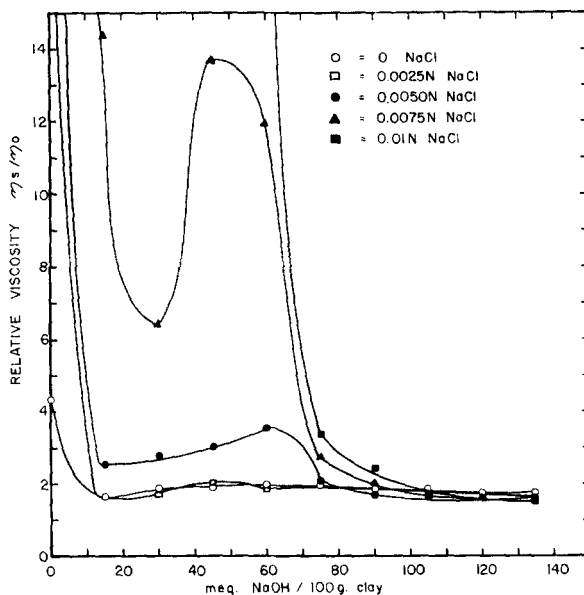


FIGURE 10.—Variation of relative viscosity of Wyoming bentonite suspensions (concentration 0.778 percent, fraction $<0.3\mu$) with increasing sodium saturation and sodium chloride concentration. The clay, prior to titration, contained an exchangeable ion ratio of 75 percent H : 25 percent Al.

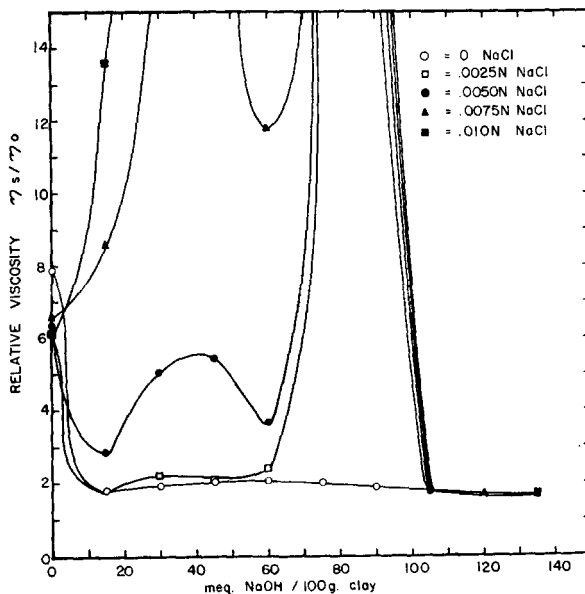


FIGURE 11.—Variation of relative viscosity of Wyoming bentonite suspensions (concentration 0.778 percent, fraction $<0.3\mu$) with increasing sodium saturation and sodium chloride concentration. The clay, prior to titration, contained an exchangeable ion ratio of 50 percent H : 50 percent Al.

viscosity with electrolyte content was obtained by adding sodium chloride to the sodium-hydrogen systems. The contrast between these curves and those presented in Fig. 6 for a hydrogen-saturated clay prepared 30 days prior to use is striking.

The viscosity of hydrogen-saturated clays is very sensitive to electrolytes. Fig. 9 shows that additions of sodium chloride greatly increase the viscosity of the hydrogen-clay. However, after about 25 percent of the hydrogen has been neutralized by sodium hydroxide, the sensitivity to electrolytes becomes relatively small. A small maximum does occur at about 60 meq/100 g of sodium hydroxide, but this is probably due to a small amount of exchangeable aluminum.

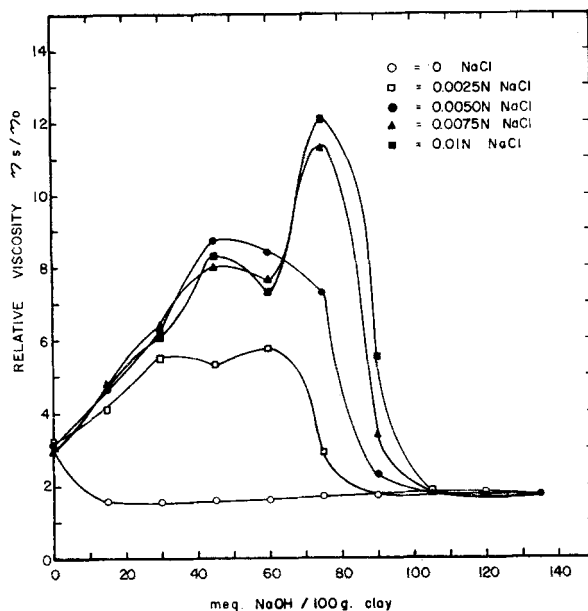


FIGURE 12.—Variation of relative viscosity of Wyoming bentonite suspensions (concentration 0.778 percent fraction $< 0.3\mu$) with increasing sodium saturation and sodium chloride concentration. The clay, prior to titration, was aluminum saturated.

The marked effect of exchangeable aluminum on the viscosity of clay suspensions in the presence of NaCl is shown in Figs. 10, 11 and 12 for varied degrees of aluminum saturation.

Fig. 10, for 25 percent aluminum-75 percent hydrogen clay, shows that the initial effect of adding sodium hydroxide is to reduce the viscosity to a minimum at all levels of sodium chloride concentrations, except for 0.01 N NaCl. At the higher concentration of sodium chloride the viscosity was too high to measure accurately, except when the exchangeable sodium exceeded 60 meq/100 g. Subsequent additions of sodium hydroxide caused the viscosity to increase to a maximum at about 50-60 meq NaOH/100 g and then decrease

to a constant level. The cation exchange capacity of this material is approximately 90 meq/100 g as determined from the titration curve.

As the aluminum content increases to 50 percent saturation (Fig. 11) there are two significant changes in the viscosity relations. First, the hydrogen-aluminum clay is very insensitive to electrolytes. With addition of sodium hydroxide the viscosity decreases to a minimum and then rises to a maximum for the low sodium chloride concentration. For the higher concentration of sodium chloride the viscosity increases directly to a maximum. The second significant difference between these curves and the preceding ones is the presence of a second maximum at about 80-90 meq NaOH/100 g.

The 100 percent aluminum-saturated clay (Fig. 12) shows about the same characteristics as the 50 percent aluminum-saturated clay, except for the decrease in the viscosity. This seemingly is due to greater flocculation and less gelation.

DISCUSSION

It is apparent from a consideration of the viscous behavior of montmorillonite suspensions that gel structures are formed under suitable conditions. The type of gel structure is most probably the brush-heap type proposed by von Nägeli in which he pictures the gel as made up of interlaced particles throughout the system and with the dispersion medium being held in the mass by capillary forces. This structure implies that the clay particles are of a heterophilic nature, i.e. the particles contain areas both of a hydrophilic character and of a hydrophobic character. If the particles were hydrophilic over the entire surface there would be no possibility of particle-to-particle contact and no structure could form. In the opposing situation, in which the surface is entirely hydrophobic, complete contact could take place and dense floccules would form when the stabilizing factors (other than solvation) were removed. In this case no structure would form. For particles of an intermediate character, it would be possible for particles to coalesce at certain points on their surface, while at the same time the adsorbed water would prevent complete flocculation and a structure would be formed throughout the suspension.

According to the picture of the gelation mechanism given above, it is obvious that the interaction of clay particles may be altered by any condition that would change the ionization of the hydrophobic part or would change the ratio of the hydrophobic to hydrophilic part. Consider the hydrogen-saturated clay. This is a heterophilic system which forms a stable suspension in the absence of electrolytes. The dual character of this system is brought out by the addition of sodium chloride, which causes an increase in viscosity. The sodium chloride reduces the ionization of the hydrophobic sites sufficiently to permit adherence of neighboring particles and some gel structure formation. The fact that complete flocculation does not occur attests to the hydrophilic character of these clay particles. While a small amount of hydrogen is probably replaced by the sodium chloride, this does not appear to be

significant since the viscosity does not decrease as in the case of exchange of hydrogen with sodium hydroxide. The replacement of only a small amount of hydrogen by sodium results in a breakdown of the gel structure and in dispersion of the clay. The addition of sodium to the clay apparently converts the clay from a heterophilic to a hydrophilic system, as indicated by the dispersion of the clay even in the presence of sodium chloride.

The calcium-saturated clay behaves somewhat like the hydrogen clay (data not shown) except that the structural formation tendencies are exhibited to a much lesser extent. The addition of sodium chloride causes only a slight increase in viscosity compared to the large change for the hydrogen system.

It is difficult to give a quantitative evaluation of the effect of ionization on the viscosity of clay suspensions. In the cases studied here it was impossible to vary the ionization without also changing some other variable (e.g. hydrogen ion saturation or clay concentration). Only in the comparison of the hydrogen-saturated and the sodium-saturated clay was it possible to show that a decrease in ionization resulted in an increased viscosity. The effect of the addition of sodium chloride on the viscosity is enlightening. There is little change in the viscosity of the clay until a certain threshold value of sodium chloride is reached. At this value the viscosity increases rapidly. Apparently, at this point the ionization, which controls the repulsive energy barrier, is reduced to such an extent that flocculation can occur. However, there are no adequate means of measuring the ionization of the clay at this high salt concentration.

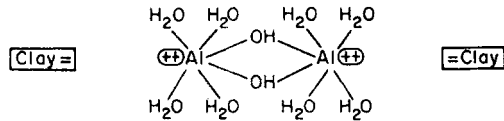
The replacement of hydrogen by aluminum on the clay results in an increase in viscosity to a maximum at about a 1 : 1 ratio of aluminum to hydrogen. As the aluminum replaces hydrogen, the clay apparently becomes more hydrophobic resulting in the formation of compact floccules at the higher aluminum content. There is seemingly an optimum ratio of hydrophobic to hydrophilic sites as far as viscosity is concerned. The fact that addition of sodium chloride to clay systems containing more than 50 percent exchangeable aluminum does not affect the viscosity indicates that the aluminum is nonionized and the clay is completely flocculated.

The influence of aluminum on the viscosity of the clay suspension may be understood by considering the reaction of Al^{3+} with sodium hydroxide. According to Russell (1950, pp. 95-97), the exchangeable aluminum on clays is in sixfold coordination with water molecules. The addition of sodium hydroxide results in replacement of part of the water by hydroxyl ions. This unit appears to be unstable and combines with another similar unit by sharing two hydroxyl ions and losing two water molecules. The over-all reaction would be



This process could continue as more hydroxyl ions are added forming large polyvalent aluminum-hydroxyl-water complex ions. Sodium ions would be adsorbed on the clay as the Al^{3+} becomes neutralized. A mechanism thus would be provided whereby clay particles could be bound together through

a bond of the type :



This bond would account for the maximum in the viscosity curve as the amount of sodium hydroxide increases. As sodium hydroxide is added in excess of that needed for complete neutralization of the Al^{3+} , aluminum hydroxide would form thereby eliminating the bonding force between the clay particles and causing the viscosity to decrease. The viscosity is not high in the absence of sodium chloride, probably owing to the dispersing action of the adsorbed sodium ions. As sodium chloride is added, the sodium ions become less ionized with a decrease in the zeta-potential and with the bonding action of the aluminum ion becoming dominant. This reaction would occur in the pH range, 4.50–5.50, and it does not explain the second maximum which occurs at higher pH values for clays containing greater than 50 percent aluminum saturation. More work is necessary before an explanation can be given.

CONCLUSIONS

From a consideration of the results of this study the following conclusions have been drawn :

(1) The viscosity of clay suspensions cannot be related directly to the ionization of the exchangeable cation. Apparently, there is an energy barrier to flocculation, and until the ionization is reduced sufficiently to overcome this energy barrier, the viscosity is practically constant with changing ionization.

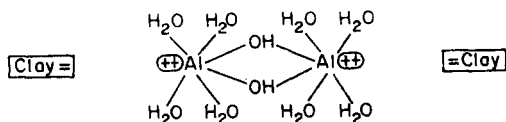
(2) The addition of sodium chloride to clay suspensions causes an increase in viscosity only after a certain threshold value is reached. This value depends upon the exchangeable cation. Below this point, addition of NaCl may cause a decrease in viscosity.

(3) An increase in clay concentration results in an increase in viscosity at a much faster rate than would be expected from consideration of the dispersed phase. Apparently interference between particles becomes dominant at higher concentrations (approximately 2 percent).

(4) The replacement of a small amount (10 percent) of hydrogen or calcium by sodium on the clay is sufficient to reduce the viscosity and disperse the clay suspension, even in the presence of 0.01 N NaCl.

(5) Aluminum ions adsorbed on the clay act as strong bonding agents between clay particles in certain pH ranges. The mechanism proposed for

this bond in this paper is of the type :



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