Flocculation Value and Gel Structure of Sodium/Calcium Montmorillonite and Illite Suspensions

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ABSTRACT

The flocculation value, the minimum salt concentration which causes flocculation within 24 hours, was determined for mixtures of Na- and Ca-montmorillonite (API-25) and Fithian illite (API-35). The equivalent fraction of exchangeable Na+, $E_{Na}$, varied from 0 to 1. We prepared Na/Ca clay suspensions by adding the appropriate amounts of homoionic dry clays to a series of Na/Ca chloride solutions (0.2 to 80 mol cnr^-3; 0.2 to 80 meq liter^-1) with appropriate sodium adsorption ratio and shaking the mixture for 1 hour. The flocculation value of Ca-montmorillonite (0.25 mol cnr^-3) increased rapidly with small amounts of exchangeable Na+: the flocculation value for an $E_{Na}$ of 0, 0.2, 0.4, and 1 was 0.25, 6, 9, and 12 mol cnr^-3, respectively. The flocculation values for Ca- and Na-illite were 0.25 and 55 mol cnr^-3, respectively, and increased linearly with $E_{Na}$. Van der Waals attraction forces are mainly responsible for flocculation of Ca-montmorillonite and illite systems. Edge-to-face attraction is dominant in flocculating Na-montmorillonite. The large effect of small amounts of exchangeable Na+ in montmorillonite suspensions results from demixing of exchangeable ions whereby Na+ is the predominant cation on the external surfaces when $E_{Na} < 0.20$.

Additional Index Words: Wyoming montmorillonite, Fithian illite, van der Waals forces, double-layer theory, (NaPO_4)_2, electrophoretic mobility, swelling pressure, sodium adsorption ratio, clay gel water content.


Recent publications report unusually large effects of low exchangeable Na+ fractions, $E_{Na}$, on the hydraulic conductivity (Frenkel et al., 1978; Pupisky and Shainberg, 1979) and on infiltration rate (Oster and Schroer, 1979) of soils leached with dilute solutions where the salt concentration was < 18 mol cm^-3 (18 meq liter^-1). Clays moved within the soil pores when $E_{Na} \leq 0.15$ and hydraulic conductivity decreased drastically within the soil layers where clay particles lodged. Infiltration rates increased, however, with irrigation water concentration at an $E_{Na}$ as low as 0.02. These results suggested that a small amount of adsorbed Na+ markedly increase the dispersivity and mobility of the clay fraction in dilute solutions.

Little information exists on clay dispersivity, or its counterpart flocculation, of mixed Na/Ca clay systems (Na/Ca indicates both Na+ and Ca^2+ are present in the exchanger phase). The minimum NaCl concentration that causes flocculation, referred to here as flocculation value, of Na montmorillonite is 12 to 16 mol cm^-3; the flocculation value for Ca montmorillonite in a CaCl_2 solution is 0.2 mol cm^-3 (van Olphen, 1977). The flocculation values of Na- and Ca-illite suspensions are 40 and 0.25 mol cm^-3, respectively (El-Swaify, 1976; Greene et al., 1978, respectively).

Sodium montmorillonite in dilute suspensions exists as single platelets (van Olphen, 1977). Calcium montmorillonite exists in packets (tactoids or quasicrystals), each consisting of several (4-9) clay platelets with a film of water 0.45 nm (4.5Å) on each internal surface.
[Norrish and Quirk (1954); Blackmore and Miller (1961)]. The illites exist in quasicrystals, regardless of the adsorbed cation (Greene et al., 1978). Using viscosity and light transmission measurements, Shainberg and Otoh (1968) found that the size of the Ca montmorillonite changes little when \( 0 < E_{Na} < 0.2 \). Higher levels of \( E_{Na} \) cause packet breakdown. Conversely, with regard to the electrophoretic mobility of Na/Ca montmorillonite, the initial increment of exchangeable Na\(^+\) increases as \( E_{Na} \) increases, although the increase in mobility (Bar-On et al., 1970). Thus, although low levels of \( E_{Na} \) do not affect the structure of the clay, they apparently do cause a large increase in clay mobility. This observation was explained by the "demixing" of the adsorbed ions in Na/Ca montmorillonite system (Shainberg and Otoh, 1968), where Ca\(^+\) is on interlayer surfaces between individual clay platelets and Na\(^+\) is on the external surface.

Because of its location, exchangeable Na\(^+\) should have a large effect on flocculation of Na/Ca systems since flocculation depends upon interactions between clay particles. In this study we evaluated the compatibility of the Na/Ca montmorillonite flocculation and "demixing" models. The results are compared also with Na/Ca illite flocculation.

**MATERIALS AND METHODS**

Clay-size fractions of Wyoming montmorillonite (API 25) and Fithian illite (API 35) were separated from larger size fractions by sedimentation. Sodium- and calcium-montmorillonite were prepared by equilibration with 1M (kmol m\(^{-3}\)) solutions of NaCl and CaCl\(_2\). Then, the clay was washed with distilled water by centrifugation until an AgNO\(_3\) test indicated that the equilibrium solution was free of Cl\(^-\). The salt-free gel was freeze-dried and stored in a desiccator. The cation exchange equilibrium solution was free of Cl\(^-\). The salt-free gel was water by centrifugation until a AgNO\(_3\) solution was 0.25 mol \( \cdot \) kg\(^{-1}\) solutions of NaCl or CaCl\(_2\) prepared by equilibration with 1M (kmol nr \( \cdot \) m\(^{-3}\)).

Fithian illite (API 35) were separated from larger size fractions by centrifugation until an AgNO\(_3\) test indicated that the equilibrium solution was free of Cl\(^-\). The salt-free gel was freeze-dried and stored in a desiccator. The cation exchange equilibrium solution was free of Cl\(^-\). The salt-free gel was water by centrifugation until a AgNO\(_3\) solution was 0.25 mol \( \cdot \) kg\(^{-1}\). Then, the clay was washed with distilled water and freeze-dried in the manner described for the montmorillonite clays. The CEC's of Na- and Ca-montmorillonite were 0.80 and 1.05 mol, kg\(^{-1}\), respectively, as determined by displacement of the exchangeable ion with 1M NH\(_4\)OAc, pH 8.3. Sodium illite was prepared by equilibrating the clay twice with 1M NaOAc solutions adjusted to a pH of 6.0 to remove the CaCO\(_3\) which contaminated the reference clay. After the Na illite was equilibrated with 1M solutions of NaCl or CaCl\(_2\), washed with distilled water and freeze-dried in the manner described for the montmorillonite clays. The CEC's of Na- and Ca-illite were 0.147 and 0.175 mol \( \cdot \) kg\(^{-1}\) respectively, after the pretreatment, as compared with 0.140 and 1.6 mol \( \cdot \) kg\(^{-1}\) before the pretreatment. Mixed Na/Ca clay suspensions with 10, 20, 40, 60, and 80% by weight of Na clay were prepared by mixing with Na or Ca chloride salt solutions with Na adsorption ratios \( R_{Na} \), of 10, 20, 40, 60, and 80, respectively. Four concentrations of montmorillonite suspensions were studied: 0.05, 0.1, 0.2, and 0.5% clay (weight of clay per unit volume of salt solution, wt/vol). The salt solution concentration ranged from 0.2 to 80 mol \( \cdot \) m\(^{-3}\), depending on the expected flocculation value. Only two concentrations of illitic suspensions were studied (0.1 and 0.2%). Based on a cation exchange equilibria study using these clays (Shainberg et al., 1980), the calculated \( E_{Na} \) for the Na/Ca-montmorillonite mixtures was about equal to 0.01 \( R_{Na} \) (±0.02) (Oster and McNeal, 1971). For illite, the selectivity for Na\(^+\) at \( R_{Na} \) values < 40 was greater than that of montmorillonite. Consequently, for \( R_{Na} \) values of 20 and 40 the corresponding \( E_{Na} \) values for illite are 0.30 and 0.46.

The flocculation value for the Na/Ca clay suspensions, as a function of concentration of the corresponding electrolyte solutions added to the clay, was measured in a series of test tubes. The contents of the tubes were mixed by shaking for 1 hour. At various time intervals after shaking, the contents of the tubes were visually inspected, and the rate of the flocculation was determined by measuring the height of the gel and of the clear solution. Both measurements were repeated 24 hours later.

The influence of 0.01, 0.1, and 1.0 mol, m\(^{-3}\) of Na polymeta-

\[ R_{Na} = C_{Na}/(C_{Na} + C_{Ca}) \]

where the ion concentrations, \( C_i \), are expressed in mol m\(^{-3}\).

**RESULTS AND DISCUSSION**

Although the primary purpose of this paper was to present the equilibrium properties of clay suspensions, several pertinent observations of the settling rate of the montmorillonite gel-water interface were made:

a) The settling rate increased with increasing salt concentration except for some suspensions with an \( E_{Na} \) of 0.40.

b) The rate decreased with increasing \( E_{Na} \).

c) The rate depended on the clay concentration in the suspension in a complicated manner. As clay concentration increased, the number of collisions increased, which increased the rate of flocculation. However, as clay concentration increased, the viscosity of the suspension also increased, leading to a slow rate of settling. Both opposing tendencies resulted in a complicated dependence of the rate on clay concentration.

d) The rate decreased exponentially with time. More than 95% of the settling occurred within 24 hours for the suspensions that did not contain metaphosphate and within 96 hours for those that did.

**Montmorillonite Suspensions**

The flocculation value of Na/Ca montmorillonite was independent of the clay concentration in the suspension, but was very sensitive to the \( R_{Na} \) of the solution phase (Fig. 1). The flocculation value for Ca-montmorillonite in CaCl\(_2\) solution was 0.25 mol \( \cdot \) m\(^{-3}\); it was 12 mol \( \cdot \) m\(^{-3}\) for Na montmorillonite. These values agree with the Schulze-Hardy valency rule of flocculation, which predicts that the monovalent and divalent colloids coagulate at concentration ratio of \((1/2)^k\) or 1:64. Our ratio was 0.25:12 or 1:48. The lack of exact agreement with the Schulze-Hardy valency rule is probably because one cannot prepare a pure homoionic montmorillonite suspension. With all phosphate (NaPO\(_4\)) on the flocculation value of 0.1 and 0.2% suspensions of Na-montmorillonite was determined using similar procedures. The NaCl concentrations ranged from 20 to 500 mol, m\(^{-3}\). Flocculation values were based on the height of the gel 96 hours after shaking rather than 24 hours. The additional time was allowed due to the slower kinetics of flocculation in the presence of metaphosphate.
the care we took in preparing Na- and Ca-montmorillonite, we know (Shainberg, 1973; Frenkel and Suarez, 1977) that in the process of removing soluble salts, some hydrolysis occurs (about 3-5%) in which the exchangeable ions are replaced by polyvalent cations (Mg$^{2+}$, Al$^{3+}$) released from the clay crystal. These cations probably make the suspensions less stable and lower the flocculation value.

It is evident from Fig. 1 that a slight addition of exchange Na$^+$ to Ca-saturated clay has a considerable effect on the flocculation value. Similar results were obtained by Bar-On et al. (1970), who measured the electrophoretic mobility of Na/Ca montmorillonite particles in distilled water suspensions. These researchers observed a large increase in electrophoretic mobility of Ca-montmorillonite with an introduction of a small amount of exchangeable Na$^+$ into the exchange complex of Ca-montmorillonite. According to the Verway and Overbeek's stability theory (van Olphen, 1977), these two properties should be interrelated. The electrophoretic mobility is a function of the electric potential at the slipping plane, zeta potential, within the diffuse double layer of the clay. A high zeta potential suggests that the double layer is more diffuse. According to the "demixing" model for adsorbed cations, Na$^+$ is the predominant cation on the external surfaces of the moving clay particles when $0.0 < E_{Na} < 0.20$, resulting in a more diffuse double layer on the external surface and a more stable suspension than if the Na$^+$ were distributed evenly over all surfaces. Consequently, higher electrolyte concentrations are required to cause flocculation.

The gel volume, expressed as a fraction of the original suspension volume, increased with the amount of clay (Fig. 2). To eliminate the effect of the amount of clay, the water content per gram of clay as a function of the $R_{Na}$ of the salt solution used to prepare the gel is presented in Fig. 3. The following features should be noted:

a) The amount of water in the Na-montmorillonite gel ranged between 215 and 280 g of water per gram of clay for the 0.3 and 0.05% suspensions, respectively. Assuming specific surface area of 750 m$^2$ g$^{-1}$ for montmorillonite, the thickness of the water film at the clay surface ranged between 290 and 370 nm (2.900 to 3.700A). The thickness of the diffuse double layer for Na montmorillonite at equilibrium with 0.012M solution of NaCl is 2.8 nm, and the range of van der Waals attraction forces does not exceed 10 nm (van Olphen, 1977). Thus it is evident that at the inter-particle distances typical for the Na-montmorillonite gel, at solution concentrations sufficient to cause flocculation, neither the diffuse double layer forces nor the van der Waals attraction were operative. Probably at these distances edge-to-face attraction forces (van Olphen, 1977) were operating.

b) The amount of water per gram of clay in the Ca-montmorillonite gel was ~ 10 g. The corresponding thickness of the water film at the clay surface is ~ 13.3 nm which is similar in magnitude to the thickness of the diffuse double layer at the flocculation concentration (0.00025 M) and to the range of the van der Waals forces. Thus, it is likely that for Ca-montmorillonite, Verway and Overbeek's theory (1948) of flocculation is applicable and the van der Waals attraction forces exceed the diffuse double-layer repulsion forces. Greene et al. (1978), studying the coagulation of montmorillonite by CaCl$_2$, arrived at a similar conclusion. They suggested that eventually quasicrystals are formed in a face-to-face association.

c) The amount of water per gram of clay in the gel increased very sharply with the introduction of exchangeable Na$^+$ into Ca montmorillonite. As is evident from Fig. 3, the amounts of water per gram of clay were 10, 50, 100, and 200 grams for gels with $R_{Na}$ of 0, 0.05, 0.10, and 0.20, respectively. The amount of water retained by the clay at $R_{Na}$ of 0.4 was identical to that of the homoionic Na clay. There is a resemblance among the amount of water in the gel (Fig. 3), the flocculation value (Fig. 1), and the electrophoretic mobility (Bar-On et al., 1970) as a function of $E_{Na}$. (Recall that the $E_{Na}$ of the mont-morillonite gels in our study are about equal to 0.01 $R_{Na}$.) Conversely, the amount of water retained by montmorillonite, at a given extraction pressure as a function of $E_{Na}$, behaves differently (Fig. 4 from Shainberg et al., 1971) when

\[ \text{Fig. 2—Effect of Na adsorption ratio and clay content (percent by weight) of the suspension on the relative gel volume of Wyoming montmorillonite (API 25). $V_r$ and $V_f$ represent the volume of gel and total volume of suspension, respectively.} \]

\[ \text{Fig. 3—Water content of Wyoming montmorillonite gel as a function of Na adsorption ratio and suspension clay content.} \]
pressure is applied. The amount of water retained by the clay does not increase with slight addition of exchangeable Na⁺. Since the introduction of a small fraction of Na⁺ into the exchange complex of Ca-quasicrystals is not sufficient to break the packets apart (Shainberg and Otoh, 1968) and the Na⁺ ions are located on the external surfaces of the crystal, the swelling pressure measurements indicated that the water retention of the clay depends more on the area of the osmotically-active surfaces (the external surfaces) than on the type of the cation on this surface. Conversely, the gel volume is very sensitive to low fraction of exchangeable Na⁺. This difficulty can be explained as follows:

The face-to-face association, typical of Ca montmorillonite, takes place only when the repulsion diffuse double-layer forces are minimal. When a small percentage of Na⁺ is introduced, it is located on the external surfaces of the Ca tactoids and, as a result, the diffuse double layers between the pockets expand and the face-to-face association becomes impossible. With the increase in the negative electrical potential at the Na-clay surfaces, however, the electrical attraction between the positive edge of one packet and the negative plane of another packet becomes stronger and the face-to-face association predominates. The open, card-house structure of edge-to-face association retains much more water than the face-to-face association of Ca montmorillonite, thus the retention curve shown in Fig. 3. When pressure is applied, the card house structure is destroyed and the amount of moisture retained as a function of \( E_{Na} \) is the one described in Fig. 4.

### Illite Suspensions

The flocculation value of Na/Ca illite as a function of \( R_{Na} \) is also presented in Fig. 1. The flocculation value of Na-illite was 4.6 times that of Na montmorillonite, whereas the flocculation values for the two Ca clays were similar. The repulsion forces for both clays in the sodium form are described and predicted by the diffuse double-layer theory (Bolt and Miller, 1955), and are similar in magnitude. Thus, the difference in the flocculation value is probably due to smaller edge-to-face attraction force in Na illite. Consideration of the exact shape of Na-illite particle explains this observation. The specific surface area of Fithian Illite is 120 m² g⁻¹, whereas that of the montmorillonite is 750 m² g⁻¹. Electronmicrographs reveal that illite particles have irregular surfaces (Green et al., 1978) and that the planar surfaces are terraced (Quirk, 1978). Upon close approach of the particles, the unavoidable mismatch of the terraces would lead to “bad” contact between the edges and the surfaces, resulting in smaller edge-to-face attraction forces, and consequently higher flocculation value for Na-illite. This hyposthesis is supported by two observations: (i) addition of peptizer, such as polymetaphosphate, which reverses the charge on the edges of Na montmorillonite, also increases the flocculation value (and is described in more detail below) and (ii) the volume of the gel in Na illite is very small (the amount of water in the sediment is about 6 g H₂O/g of clay) suggesting that the card house structure typical to Na montmorillonite is not as stable.

With increase in \( R_{Na} \) of Na/Ca illite system, the flocculation value is increased (Fig. 1). However, the effect of Na in the illite suspensions follows more closely a simple linear relationship than for montmorillonite suspensions. If the flocculation values were plotted as a function of \( E_{Na} \) rather than \( R_{Na} \), the montmorillonite line in Fig. 1 would not change, whereas that for illite would become more linear. As mentioned earlier, the selectivity for exchangeable Na⁺ was greater for illite than for montmorillonite. This observation suggested that “demixing” of the adsorbed cations observed in Na/Ca montmorillonite is not as pronounced in Na/Ca illite suspension, which is probably the result of the absence of interlayer exchange sites for illite. Our data for illite were different than those reported by Arora and Coleman (1979) for an illite obtained from Morris, IL (API-36) which also is reported to contain carbonaceous impurities (Kerr et al., 1949). They obtained a concave relationship, with respect to the abscissa, between the salt concentration required to prevent dispersion and \( R_{Na} \). At \( R_{Na} \) values of 0, 30, 60, and \( \infty \), the corresponding salt concentrations were 0.5, 30, 42, and 185 mol., m⁻³.

We obtained similar results with Na/Ca Fithian Illite suspensions made from “homoionic” clays that were not pretreated with the NaOAc-HOAc buffer solutions to remove lime. Lime dissolution during the flocculation experiment would lower \( E_{Na} \) and the flocculation value.

Illitic clays with low \( E_{Na} \) were more easily dispersed.
than the corresponding montmorillonite clays. The flocculation value for Na/Ca montmorillonite with an $E_{Na}$ of 0.1, 0.2, and 0.3 was 4.0, 7.0, and 8.5 mol·m$^{-3}$, respectively, whereas for Na/Ca illite suspensions, the flocculation value was 10, 18, and 24 mol·m$^{-3}$, respectively. This observation suggested that soil with illitic clays is more sensitive to dispersion and clay movement than is soil with montmorillonite clays.

The Effect of Peptizing Agent

The effect of Na polymetaphosphate ($\text{NaPO}_3)_3$ on the flocculation value and the gel volume of Na montmorillonite in NaCl solutions is summarized in Table 1. The flocculation values of the peptizer-treated suspensions increases rapidly with increasing peptizer concentration. An explanation was given by van Olphen (1977). Considering the effectiveness of the polymetaphosphate in low concentration, he suggested that the anions are chemisorbed at the edges of the clay particles by reacting with the exposed Al. Thus, the charge of the edges becomes negative, which prevents the edge-to-face bond from taking place.

If the edge-to-face bond is eliminated by the adsorption of the polymetaphosphate, then one might expect that the open, card-house structure of the gel should also be eliminated. It is evident from Table 1 that the peptizer treated Na-montmorillonite gel still maintains the open structure. Van Olphen (1977) also reported that the flocculation value of Na-montmorillonite increased with the concentration of Na-polymer up to 340 mol·m$^{-3}$ of NaCl in 100 mol·m$^{-3}$ (NaPO$_3$)$_3$ suspensions. It does not seem likely that adsorption on the positive edges can explain the effect of the peptizer at the high concentration range. Thus, it seems to us that hydroxylaluminum polymers, present in the Na-montmorillonite suspensions as a result of weathering and dissolution, behave as cementing materials and thereby affect the flocculation process. Complexation of the polyvalent Al ions stabilize the clay in suspension.

CONCLUSION

The dispersivity of montmorillonite and illite clay is very sensitive to a low fraction of Na in the exchange complex. Whereas the flocculation value of both Ca clays is 0.25 mol·m$^{-3}$, the flocculation values of clays with an $E_{Na}$ of 0.20 is 7.0 and 18.0 mol·m$^{-3}$ for montmorillonite and illite clays, respectively. Van der Waals attraction forces are the main forces responsible for flocculation in Ca-montmorillonite and illite systems. The edge-to-face attraction plays a dominant role in the gel formation of Na montmorillonite. The high dispersivity of the clays in the presence of a low percentage of exchangeable Na explains the high sensitivity of soils with low $E_{Na}$ to leaching with dilute solutions and distilled water.

LITERATURE CITED