RHEOLOGICAL BEHAVIOR OF Na-MONTMORILLONITE SUSPENSIONS AT LOW ELECTROLYTE CONCENTRATION

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Abstract—The prevailing concept that positive-edge to negative-face attraction accounts for the rheological behavior of montmorillonite suspensions at low electrolyte concentration was investigated. In one experiment, Mg^{2+} released from Na-montmorillonite was measured at several NaCl concentrations; in a second experiment, the viscosity, η, and the extrapolated shear stress, θ, were measured at several clay concentrations, pHs, and NaCl concentrations; and in a third experiment, the absorbance, A, was measured at two wavelengths (450 and 760 nm) at different clay and electrolyte concentrations. The released Mg^{2+} decreased with increasing NaCl concentration until it became zero at a NaCl concentration between 0.01 and 0.02 M, depending on pH. Thereafter, it increased with increasing NaCl concentration. Both θ and η were highly correlated with the amount of released Mg^{2+}. Also, A remained constant until the NaCl concentration corresponded to that at the minimum of θ. Thereafter, it increased and became linearly related to θ. These results suggest: (1) positive-edge to negative-face interaction cannot solely account for the rheological properties of montmorillonite at low electrolyte concentration, and (2) the release of octahedral Mg^{2+} from montmorillonite affects θ, because it reduces the negative charge on the particles and, thereby, the repulsive force between them.

Key Words—Electrolyte, Montmorillonite, Particle attraction, Rheology, Shear, Viscosity.

INTRODUCTION

Montmorillonite-water mixtures exhibit unusual rheological behavior at low electrolyte concentrations. For example, extrapolated shear stress falls to a minimum with increasing electrolyte concentration and then rises (van Olphen, 1956; Rand *et al.*, 1980). van Olphen (1956, 1977) ascribed this behavior to the opposite effects of electrolyte concentration on two kinds of particle-particle interactions, namely, electrical attraction between positively charged edges and negatively charged surfaces, and electrical repulsion between edges and/or surfaces of like charge. According to double-layer theory (Verwey and Overbeek, 1948; van Olphen, 1977), both kinds of interaction decrease with increasing electrolyte concentration. On the other hand, van der Waals attraction remains constant. Below a certain electrolyte concentration, the positive-edge negative-surface attraction is supposed to predominate, but above this concentration, van der Waals attraction is supposed to predominate. The net result is that the overall attractive force between particles decreases to a minimum with increasing electrolyte concentration and then increases. The foregoing explanation is questionable, however, because substantial evidence exists that suggests that the edges of montmorillonite particles are not positively charged at any pH (M'Ewen and Pratt, 1957; M'Ewen and Mould, 1957; Low, 1968; Rand *et al.*, 1980; Tessier and Pedro, 1982). Further, it is known that H^+ displaces Al^{3+} and Mg^{2+} from octahedral sites in a montmorillonite layer (Low, 1955; Barshad, 1960;

Eeckman and Laudelout, 1960; Coleman and Craig, 1961; Miller, 1965) and that, because of hydrolysis, this displacement can occur when the electrolyte concentration is low, even if the montmorillonite is initially Na-saturated (Kamil and Shainberg, 1968; Shainberg, 1973; Shainberg *et al.*, 1974; Frenkel and Suarez, 1977). The possibility exists, therefore, that changes in rheological properties with electrolyte concentration at low electrolyte concentrations are related to the displacement of octahedral Al^{3+} and Mg^{2+} from the montmorillonite crystal. To test this possibility, the present investigation was conducted.

MATERIALS AND METHODS

Interparticle forces in clay suspensions can be studied in different ways. We chose to study them by observing how changes in electrolyte concentration and pH affected the rheology of the suspensions and their absorbance, i.e., scattering of light.

The clay used for the present experiments was Na-saturated, <2-μm montmorillonite from Upton, Wyoming. It was prepared as described by Low (1980). For the rheological measurements, the clay was suspended at a concentration of 2% w/w in solutions containing different concentrations of NaCl. Each suspension was prepared by mixing 0.8 g of clay with 20 ml of distilled water, allowing the suspension to stand overnight, adding 20 ml of a NaCl solution at a given concentration, and equilibrating for one day in a water bath at 20°C. When prepared in this way, the pH of the different suspensions decreased with increasing NaCl concentration and ranged from 8.5 to 7.0. In some experiments, we were interested in controlling the pH.

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Here, HCl or NaOH was added in appropriate amounts until the pH was stabilized at the desired value, a process that required about two weeks. The added NaOH or HCl was subsequently included in the calculation of the final electrolyte concentration.

The relation between the shear stress, s, and the shear rate, σ, was determined for each suspension in a Fann V-G (Model 35) viscometer. This viscometer was described in detail by Savins and Roper (1954). It was calibrated initially by using glycerin solutions of known viscosity. During a measurement, the glycerin or clay suspension was kept at 20°C by immersing the cup of the viscometer in a water bath at that temperature.

After the rheological measurements were completed, the suspensions were centrifuged at 30,000 rpm for 60 min, and the supernatant solutions were analyzed for Mg^{2+} by means of a Jarrell Ash Absorption Spectrophotometer.

For absorbance measurements, suspensions containing the clay at concentrations of 0.2, 0.5, and 0.6% w/w and NaCl at several different concentrations were prepared essentially as described above. The absorbance, A, was then determined at wavelengths of 450 and 760 nm by means of a Cary 17D spectrophotometer. Only results for 450 nm are presented inasmuch as both wavelengths produced similar curves. At these wavelengths, the clay particles do not absorb the radiation (Banin, 1968).

Absorbance, A, is defined by means of the equation

$$2.303 \log(I_0/I) = \tau l = 2.303 \text{ A}, \tag{1}$$

where I_0 and I are the intensities of the incident and transmitted radiation, respectively, τ is the turbidity, and l is the path length. According to the Raleigh equation,

$$\tau = kNV^2, \tag{2}$$

where N is the number of scattering units (discrete particles or flocs) per cm³, V is the volume of the scattering units, and k is an optical constant. Combination of Eqs. (1) and (2) gives

$$A = kNV^2l/2.303. \tag{3}$$

Hence, A can be used as an indication of the degree of flocculation.

THEORETICAL CONSIDERATIONS

Regardless of their mutual arrangement, clay particles are subject to attractive and repulsive forces that fall off with interparticle distance at different rates. As a result, the net energy of interaction between the particles rises (becomes more positive) as they approach each other until a maximum is reached. Then it falls rapidly to a negative minimum and rises again thereafter to relatively high positive values. Consequently, the curve of interaction energy vs. interparticle distance exhibits an energy barrier followed by an energy well.

If the particles are beyond the energy barrier, they are in the dispersed state; whereas, if they are in the energy well, they are in the flocculated state. As the energy well deepens, an increasingly larger fraction of the particles will be in the flocculated state. Moreover, as it deepens, the energy required to separate or disperse the particles will increase. This energy can be regarded as the bond energy that holds the particles together.

If a clay suspension is undergoing shear at any given shear rate, bonds between the flow units (individual particles or flocs) are constantly being broken and reformed. At relatively high shear rates, the relation between the shear stress, s, and the shear rate, σ, becomes linear and is described by the equation

$$s = \eta\sigma + \theta, \tag{4}$$

where η is the plastic viscosity and θ is the Bingham yield value or extrapolated sheer stress. Note that η is the slope of the linear relation between s and σ and θ is its intersection with the s-axis. Here, the resistance of the suspension to flow can be considered as consisting of two parts, a Newtonian part in which the shear stress is proportional to the shear rate and a non-Newtonian part in which the shear stress is constant irrespective of the shear rate. The Newtonian part has been ascribed to hydrodynamic effects produced by flow of the fluid around the flow units, and the non-Newtonian part has been ascribed to interaction between the flow units (e.g., Hunter and Nicol, 1968). According to rheological theory (Goodeve, 1939, 1949; Gillespie, 1960),

$$\theta = E_A K_1 N^2/2, \tag{5}$$

where E_A is the bond energy between the flow units, K_1 is a constant, and N is the number of flow units per cubic centimeter. If the flow units are assumed to be spherical, as a floc may be, it can be shown (Gillespie, 1960) that Eq. (5) can be transformed to

$$\theta = 3E_A\phi^2/\pi^2a^3, \tag{6}$$

where ϕ is the volume fraction of the flow units whose radius is a.

RESULTS AND DISCUSSION

Typical curves of s vs. σ are shown in Figure 1 for the Na-Upton montmorillonite suspensions at a pH of 7.0, a montmorillonite concentration, C_c, of 2% w/w, and different values of the NaCl concentration, C_{NaCl}. Similar curves of s vs. σ were obtained at pH values of 4.0 and 10.0.

Curves of θ vs. C_{NaCl} and η vs C_{NaCl} are shown in Figures 2 and 3, respectively. Similar curves of θ vs. C_{NaCl} were obtained by van Olphen (1956) and Rand et al. (1980). Observe that the curves in Figures 2 and 3 closely resemble each other and that the minimum in both occurs at $C_{NaCl} = 5 \times 10^{-3}$ M. Evidently, θ and η are highly correlated. Because, in keeping with Eqs.
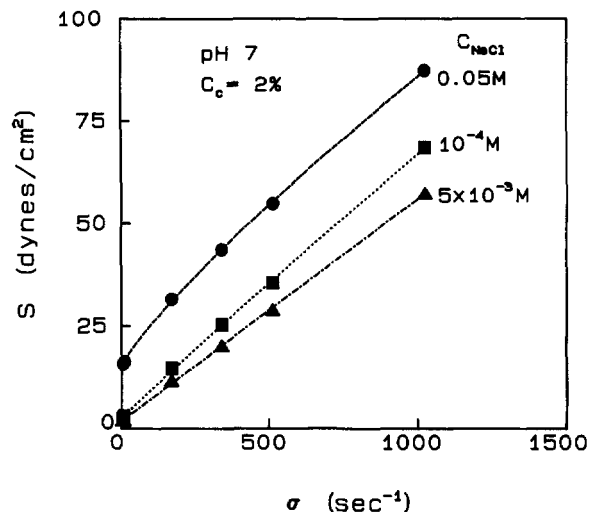
Figure 1. Relation between shear stress, s, and shear rate, σ, for 2% suspensions of Na-montmorillonite at three electrolyte concentrations and a pH of 7.0

(5) and (6), θ is supposed to depend on the strength of the bonds between the flow units, this correlation suggests that η also depends on the strength of these bonds and that the first term in Eq. (4) is not entirely ascribable to hydrodynamic effects. In view of the existing correlation between θ and η, the data for both of them need not be discussed; only the data for θ will be discussed hereafter.
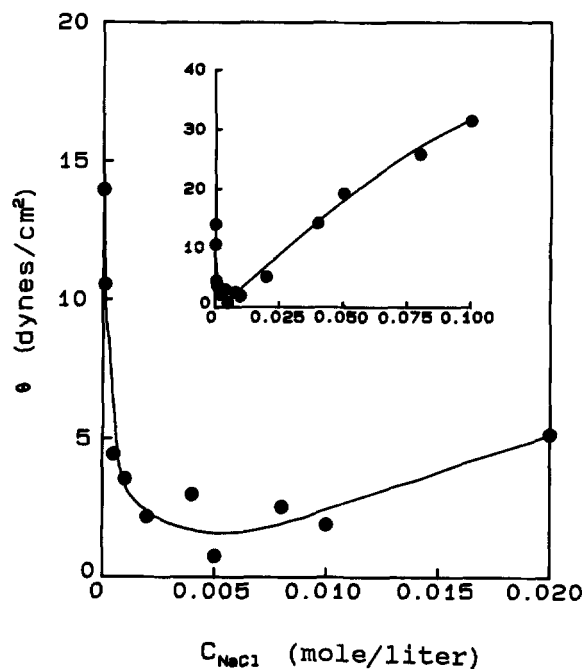
Figure 2. Relation between extrapolated shear stress, θ, and NaCl concentration, C_{NaCl}, for a 2% suspension of Na-montmorillonite.
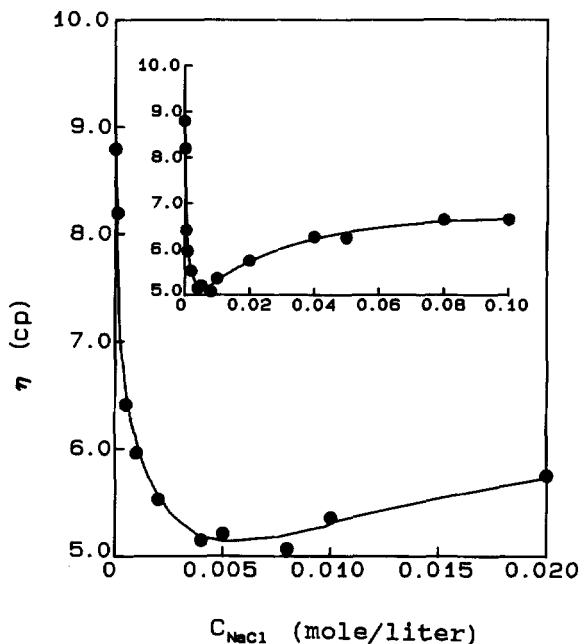
Figure 3. Relation between plastic viscosity, η, and NaCl concentration, C_{NaCl}, for a 2% suspension of Na-montmorillonite.

Figure 4 shows the relation between absorbance, A, and NaCl concentration. Observe from this illustration that A (and, hence, the degree of dispersion) was constant until the concentration of NaCl exceeded $\sim 10^{-3}$ M. Thereafter, it began to increase. Norrish (1954) and Foster *et al.* (1955) observed by means of X-ray powder diffraction that the c-axis spacing of Na-saturated montmorillonite in NaCl solutions decreased progressively with the NaCl concentration until a concentration of 0.25 M was reached. It then decreased abruptly from ~ 40 to 19 Å. The c-axis spacing of montmorillonite cannot be measured unless its layers are in a periodic, parallel (i.e., face-to-face) arrangement. Moreover, an abrupt decrease in c-axis spacing would not have occurred unless the layers jumped into an energy well. According to the theory of flocculation (Reerink and Overbeek, 1954; Ottewill *et al.,* 1960), flocculation is the result of such a jump. Thus, Na-montmorillonite does not begin to flocculate in the face-to-face arrangement until the NaCl concentration reaches ~ 0.25 M. This means that the flocculation that began at $\sim 10^{-3}$ M was not in the face-to-face arrangement, and must have been in the edge-to-edge or edge-to-face arrangement.

Comparison of Figures 2 and 4 shows that θ changed with NaCl concentration but, below a concentration of 10^{-3} M, A (and, hence, N) did not. In view of Eq. (5), these results suggest that the decrease in θ with increasing C_{NaCl} was due to a corresponding decrease in E_A.
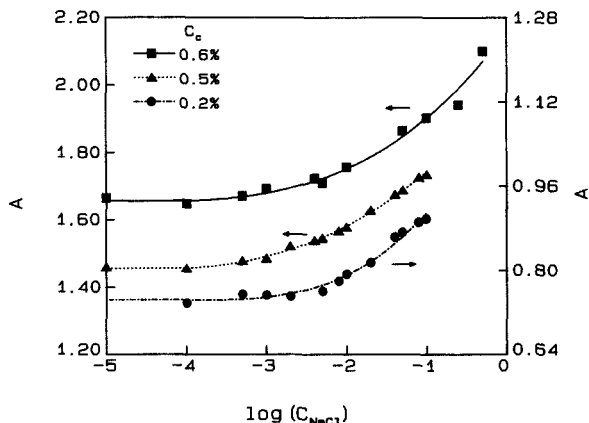
The constancy of A in the range of NaCl concentra-

Figure 7. Relation between extrapolated shear stress, θ, and absorbance, A, for a 0.6% suspension of Na-montmorillonite at different NaCl concentrations $>5 \times 10^{-3}$ M.

are strikingly similar, which suggests that the magnitude of θ was controlled by the release of Mg^{2+} from the montmorillonite crystal. Although the released Mg^{2+} was only a small fraction of the octahedral Mg^{2+} that was present ($<2\%$), its loss from crystal edges could have had a profound effect on their character and, thereby, on their mutual interaction. More will be said of this below.

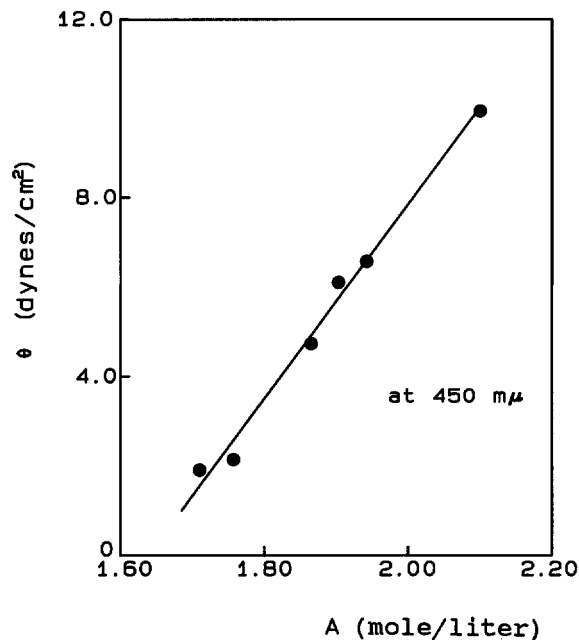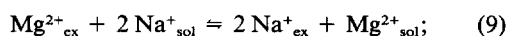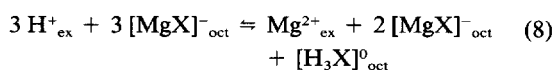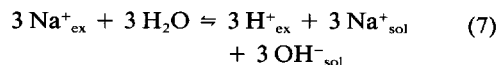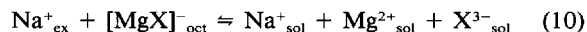The fact that flocculation increases as the strength of the interparticle bonds increases was noted above. Flocculation enhances the magnitude of V in Eq. (3) and, hence, the magnitude of A as well. Moreover, as the strength of the interparticle bonds increases, E_A increases and, in keeping with Eq. (5), θ increases accordingly. Therefore, it was of interest to determine whether or not A and θ were related after the onset of flocculation at $C_{NaCl} = 5 \times 10^{-3}$ M. For this purpose, Figure 7 was constructed. Note that θ and A are linearly related. A similar relation was observed by Neumann and Sansom (1971), who also observed that this relation was not affected by the nature of the exchangeable cation. Recall that θ and η were highly correlated. Therefore, A may possibly serve as a criterion of the rheological behavior of clay suspensions.

On the basis of our results, we conclude that positive-edge to negative-surface attraction cannot account for the effect of electrolyte on the rheological behavior of montmorillonite suspensions, as previously supposed. The same conclusion was reached by Rand et al. (1980). Our results, however, may be explained by hypothe-

sizing that Mg^{2+} was released by two primary mechanisms: (1) by the hydrolytic replacement of exchangeable Na^+ by H^+ followed by the substitution of three exchangeable H^+ for each Mg^{2+} in octahedral sites originally occupied by Al^{3+}; and (2) by decomposition of regions of the crystal, especially edges and corners that have been destabilized by the substitution of Mg^{2+} for Al^{3+}. The first mechanism involves the reactions:

$$3\,Na^+_{ex} + 3\,H_2O \rightleftharpoons 3\,H^+_{ex} + 3\,Na^+_{sol} \qquad (7)$$
$$+ \; 3\,OH^-_{sol}$$

$$3\,H^+_{ex} + 3\,[MgX]^-_{oct} \rightleftharpoons Mg^{2+}_{ex} + 2\,[MgX]^-_{oct} \qquad (8)$$
$$+ \; [H_3X]^0_{oct}$$

$$Mg^{2+}_{ex} + 2\,Na^+_{sol} \rightleftharpoons 2\,Na^+_{ex} + Mg^{2+}_{sol}; \qquad (9)$$

whereas, the second mechanism involves the reactions

$$Na^+_{ex} + [MgX]^-_{oct} \rightleftharpoons Na^+_{sol} + Mg^{2+}_{sol} + X^{3-}_{sol} \qquad (10)$$

$$Mg^{2+}_{sol} + 2\,Na^+_{ex} \rightleftharpoons Mg^{2+}_{ex} + 2\,Na^+_{sol}. \qquad (11)$$

In these reactions, the subscript ex denotes an ion that is adsorbed on the exchange complex, the subscript sol denotes an ion that is dissolved in the solution, and the square brackets with the subscript oct denotes the complex formed by the octahedral cation and surrounding structure, X, with which it is coordinated.

Release of Mg^{2+} by the first mechanism decreased with increasing NaCl concentration because conversion of the Na-montmorillonite to H-montmorillonite by hydrolysis was inhibited, and, hence, fewer exchangeable H^+ were available to substitute for the octahedral Mg^{2+} (Shainberg, 1973; Shainberg et al., 1974; Frenkel and Suarez, 1977). Release of Mg^{2+} by the second mechanism increased with increasing NaCl concentration because the solubility of the crystal, specially of its unstable regions, increased with increasing ionic strength (Glasstone, 1946). The net result was that the release of octahedral Mg^{2+} fell to a minimum and rose thereafter with increasing NaCl concentration. Note from Eqs. (8) and (10) that both mechanisms reduced the negative charge on the montmorillonite layers. This is consistent with the observation of Frenkel and Suarez (1977) that Mg^{2+} release is accompanied by a decrease in cation-exchange capacity. Also note that both mechanisms increased the exchangeable Mg^{2+}. A reduction in negative charge would increase the tendency for flocculation. The same is true of an increase in exchangeable Mg^{2+}. Recall that the degree of flocculation and θ both depend on the strength of interparticle bonds. Thus, θ was directly correlated with Mg^{2+} release. Of course, the final rise in θ was also promoted by the added electrolyte because it reduced

the overlap of electrical double layers and/or hydration shells.

ACKNOWLEDGMENTS

REFERENCES

Akae, T. and Low, P. F. (1988) Interparticle bond energy and rheological properties of clay suspensions: *J. Colloid Interface Sci.* (in press).

Banin, A. (1968) Ion exchange isotherms of montmorillonite and structural factors affecting them: *Israel J. Chem.* **6**, 27–36.

Barshad, I. (1960) Significance of the presence of exchangeable magnesium ions in acidified clays: *Science* **131**, 988–990.

Cebula, D. J. and Ottewill, R. H. (1981) Neutron diffraction studied on lithium montmorillonite-water dispersions: *Clays & Clay Minerals* **29**, 73–75.

Coleman, N. T. and Craig, D. (1961) The spontaneous alteration of hydrogen clay: *Soil Sci.* **9**, 14–18.

Eeckman, J. P. and Laudelot, H. (1960) Chemical stability of hydrogen-montmorillonite suspensions: *Kolloid-Zeitschrift* **178**, 99–107.

Foster, W. R., Savings, J. G., and Waite, J. M. (1955) Lattice expansion and rheological behavior relationships in water-montmorillonite systems: in *Clays and Clay Minerals. Proc. 3rd Natl. Conf., Houston, Texas, 1954,* W. E. Milligan, ed., *Natl. Acad. Sci. Natl. Res. Conf. Publ.* **395**, Washington, D.C., 296–316.

Frenkel, H. and Suarez, D. L. (1977) Hydrolysis and decomposition of calcium montmorillonite: *Soil Sci. Soc. Amer. J.* **41**, 887–891.

Gillespie, T. (1960) An extension of Goodeve's impulse theory of viscosity to pseudoplastic systems: *J. Colloid Sci.* **15**, 219–231.

Glasstone, S. (1946) *Textbook of Physical Chemistry:* van Nostrand, New York, 961–963.

Goodeve, C. F. (1939) A general theory of thixotropy and viscosity: *Trans. Faraday Soc.* **35**, 342–358.

Goodeve, S. R. (1949) The mechanism of thixotropic and plastic flow: in *Proc. Int. Rheol. Congr. (Holland), 1948, Part 2:* North Holland Publishing, Amsterdam, 5–11.

Hunter, R. J. and Nicol, S. K. (1968) The dependence of plastic flow behavior of clay suspension on surface properties: *J. Colloid Interface Sci.* **28**, 250–259.

Kamil, J. and Shainberg, I. (1968) Hydrolysis of sodium montmorillonite in sodium chloride solutions: *Soil Sci.* **106**, 193–199.

Low, P. F. (1955) The role of aluminum in the titration of bentonite: *Soil Sci. Soc. Amer. Proc.* **19**, 135–139.

Low, P. F. (1968) Mineralogical data requirements in soil physical investigations: in *Mineralogy in Soil Science and Engineering,* Soil Science Society of America Special Publication No. 3, Madison, Wisconsin, 1–34.

Low, P. F. (1980) The swelling of clay: II. Montmorillonite: *Soil Sci. Soc. Amer. J.* **44**, 667–676.

M'Ewen, M. B. and Mould, D. L. (1957) Gelation of montmorillonite, II. The nature of the interparticle forces in soils of Wyoming bentonite: *Trans. Faraday Soc.* **53**, 548–564.

M'Ewen, M. B. and Pratt, M. I. (1957) The gelation of montmorillonite, I. The formation of a structural framework in soils of Wyoming bentonite: *Trans. Faraday Soc.* **53**, 535–547.

Miller, R. J. (1965) Mechanisms for hydrogen to aluminum transformations of clays: *Soil Sci. Soc. Amer. Proc.* **29**, 36–39.

Neumann, B. S. and Sansom, K. G. (1971) The rheological properties of dispersions of laponite, a synthetic hectorite-like clay, in electrolyte solutions: *Clay Miner.* **9**, 231–243.

Norrish, K. (1954) The swelling of montmorillonite: *Disc. Faraday Soc.* **18**, 120–134.

Ottewill, R. H., Rastogi, M. C., and Watanabe, A. (1960) Stability of hydrophobic sols in the presence of surface active agents, I. Theoretical treatment: *Trans. Faraday Soc.* **56**, 854–865.

Rand, B., Pekenc, E., Goodwin, J. W., and Smith, R. B. (1980) Investigation into the existence of edge-face coagulated structures in Na-montmorillonite suspensions: *J. Chem. Soc. Faraday Trans.* **76**, 225–235.

Reerink, H. and Overbeek, J. Th. G. (1954) The rate of coagulation as a measure of the stability of silver iodide sols: *Disc. Faraday Soc.* **18**, 74–84.

Savins, J. G. and Roper, W. F. (1954) A direct-indicating viscometer for drilling fluids: *Proc. Amer. Petrol. Inst., Sect. IV*, 7–22.

Schofield, R. K. and Samson, H. R. (1953) The deflocculation of kaolinite suspensions and the accompanying change-over from positive to negative chloride adsorption: *Clay Minerals Bull.* **2**, 45–51.

Shainberg, I. (1973) Rate and mechanism of Na-montmorillonite hydrolysis in suspensions: *Soil Sci. Soc. Amer. Proc.* **37**, 689–694.

Shainberg, I., Low, P. F., and Kafkafi, U. (1974) Electrochemistry of sodium-montmorillonite suspension: I. Chemical stability of montmorillonite: *Soil Sci. Soc. Amer. Proc.* **38**, 751–755.

Tessier, D. and Pedro, G. (1982) Electron microscopy study of Na smectite fabric-role of layer charge, salt concentration, and suction parameters: in *Proc. Intl. Clay Conf., Bologna and Pavia, 1981,* H. van Olphen and F. Veniale, eds., Elsevier, Amsterdam, 145–176.

van Olphen, H. (1956) Forces between suspended bentonite particles: in *Clays and Clays Minerals. Proc. 4th Natl. Conf., University Park, Pennsylvania, 1956,* Natl. Res. Council Natl. Acad. Sci. Publ. **456**, Washington, D.C., 204–224.

van Olphen, H. (1977) *Clay Colloid Chemistry:* 2nd ed., Wiley, New York, 318 pp.

Verway, E. J. W. and Overbeek, J. Th. G. (1948) *Theory of the Stability of Lyophobic Colloids:* Elsevier, New York, 205 pp.

Vold, M. J. (1957) The van der Waals' interaction of anisometric colloidal particles: *Proc. Indian. Acad. Sci.* **46A**, 152–156.