

FLOW PROPERTIES OF DILUTE MONTMORILLONITE DISPERSIONS

by

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ABSTRACT

A viscometric study of dilute montmorillonite dispersions, using for the most part dilution-type capillary viscometers supplemented by a falling-head capillary viscometer, has involved a determination of the concentration dependence of viscosity of such dispersions in both distilled and electrolyte-containing water. The results of the study have been interpreted in terms of a theory of incremental viscosity, and of the Schulz-Blaschke (1941) equation. Use of this equation yields good extrapolations to zero concentration for the determination of limiting viscosity number, and permits calculation of "interaction indices" which are considered, for reasons discussed in detail, to be a measure of particle-particle interaction. These indices are related to the cationic heat of hydration of the electrolyte used, and relationship is demonstrated between the yield stress of a 3 percent montmorillonite-electrolyte-water system and such interaction indices. The recent work of Packter (1956, 1957) is discussed, and the relation of the results of this investigation to the data of van Olphen (1956, p. 204) is noted.

INTRODUCTION

In recent years, a number of excellent papers on the properties of the system montmorillonite-water have appeared in the clay literature. Of particular interest are the series of papers by van Olphen (1951; 1954; 1956; 1957) and the various publications of Norrish (1954), Foster, Savins, and Waite (1955), M'Ewen and Pratt (1957), M'Ewen and Mould (1957), and Packter (1956; 1957). These contributions are of particular value in the interpretation of the observed phenomena in this system.

The present paper presents the results of a continuing study of the flow properties of dilute montmorillonite dispersions in fresh and in electrolyte-containing water. The presentation will involve a discussion of the experimental techniques, followed by a detailed analysis of the experimental results and a consideration of various methods of presenting data from viscometric studies of clay-water systems. Particular emphasis will be placed on the Schulz-Blaschke (1941) equation and an attempt will be made to correlate interaction indices obtained from this equation with the properties of a bentonite gel.

It should be pointed out here that, in the application of the Schulz-Blaschke equation and the calculation of interaction indices from viscometric data on dilute montmorillonite-water systems, the recent papers by Packter (1956; 1957) have priority and have anticipated much of the author's work.

This fact was pointed out in correspondence with the Clay Conference program committee, but the decision was to permit presentation of this paper. This paper, however, will demonstrate the reason why the Schulz-Blaschke treatment fits the data and will set forth the equation in a way different from that of Packter (1956).

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Nomenclature

η	=	viscosity of system
η_0	=	viscosity of bulk phase
ϕ_v	=	volume fraction
η_{rel}	=	η/η_0 = relative viscosity
η_{sp}	=	$\eta/\eta_0 - 1 = \eta_{rel} - 1$ = specific viscosity
η_{sp}/ϕ_v	=	viscosity number
$[\eta]$	=	$\lim_{\phi_v \rightarrow 0} (\eta_{sp}/\phi_v)$
k	=	interaction index
$J_{ov}\rho$	=	axial ratio (ratio of major to minor axes of hypothetical ellipsoid)

EXPERIMENTAL METHODS

The montmorillonite used in this study, supplied by Baroid Division, National Lead Company, Houston, Texas, had been highly beneficiated by multiple stage centrifugation. This operation involved the removal in several stages of the coarse end of the product from the preceding stage. Thus, the final fraction contained all the "fine" clay ($<0.8\mu$) present in the original sample. The exchange properties of the final material were as follows: C.E.C., 96 meq/100 g of clay; exchangeable Na^+ , 80 meq/100 g; exchangeable Ca^{2+} , ~ 20 meq/100 g; and soluble Ca^{2+} and Mg^{2+} , about 35 meq/100 g. The preparative technique involved the preparation of fresh water dispersions using the Waring Blender. In general, the initial preparation contained about 1 percent clay and this stock sample was then diluted with water to various concentration levels. The electrolyte-containing systems were obtained by adding electrolyte to a montmorillonite dispersion in fresh water to a known concentration of electrolyte. Dilutions were then carried out using electrolyte solutions of the same ionic strength.

The viscometric data were obtained using either capillary viscometers or the falling head viscometer described by Wood, Granquist and Krieger (1956). Clay concentrations in the fresh water dispersions were determined gravimetrically (constant weight at 110°C). The same dilution techniques were used in the preparation of the electrolyte-containing systems, and the clay concentrations in these systems were calculated from the fresh water data. Volume fractions were calculated on the basis of a density of 2.4 for the clay and 1.0 for the water and on tabulated density for the particular electrolyte concentration being employed. No attempt was made to correct this volume fraction to a hydrodynamic volume by making assumptions as to the extent of the solvation layer of the particular "hydrodynamic

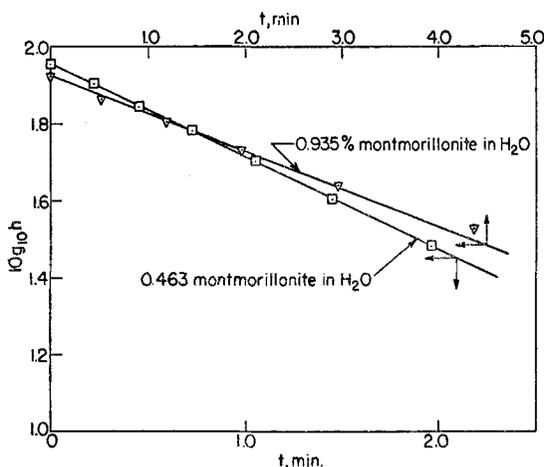


FIGURE 1.—Method of plotting falling-head viscometer data.

particle". This procedure can be justified on the basis that neglect of solvation in the calculation of volume fraction will be compensated in the observed values of interaction index.

The viscosities of the water and electrolyte solutions were determined carefully and the system viscosities were converted to relative and specific viscosities. The falling head viscometer was used to check the capillary viscometer to make certain that the viscometric data were obtained in a region of Newtonian flow. At the lower dilutions, the systems are Newtonian, but at clay concentrations near 1 percent non-Newtonian behavior is observed at low rates of shear.

The operation of the falling head viscometer was described in the earlier publication (Wood, Granquist and Krieger, 1956), and Fig. 1 is presented to show the type of data obtained in this particular study. Figure 1 plots $\log_{10} h$ (effective height) vs. the total elapsed time of flow. Linearity is indicative of Newtonian flow while deviation from the straight line shown indicates the beginning of a non-Newtonian region. This can be seen in the

low shear-stress region (large flow times) of the 0.935 percent montmorillonite dispersion.

These viscometric data were examined by a theory of incremental viscosity and by the Schulz-Blaschke equation, and the data from these equations were used to calculate a shape factor or axial ratio from the equations of Kuhn (1933) and Simha (1940).

DISCUSSION OF RESULTS

The usual procedure for presenting viscometric data is to plot the viscosity number as a function of the volume fraction. Actually this method is applicable only in extremely dilute solutions, and such a functional dependence demands that the total viscosity effect observed is the sum of the effects caused by each individual suspended particle. That is, consider the viscosity of the system after such an incremental addition to be the result of adding the increment to a pure bulk phase having a viscosity equal to that possessed by the system just prior to the addition. The applicability of such a first power plot to a particular system can be determined readily through a method of presentation of the data resulting from such an incremental viscosity approach, as follows :

$$\begin{aligned}d\eta &= A\eta d\phi_v \\ \int_{\eta_0}^{\eta} \frac{d\eta}{\eta} &= A \int_0^{\phi_v} d\phi_v \\ \ln \frac{\eta}{\eta_0} &= A\phi_v \\ \frac{\ln \eta_{\text{rel}}}{\phi_v} &= A\end{aligned}$$

Thus, a plot of

$$\frac{\ln \eta_{\text{rel}}}{\phi_v} \text{ vs. } \phi_v$$

should be a straight line parallel to the volume concentration axis. In Fig. 2 such plots are presented for a dispersion of montmorillonite in water and in 1.0 M sodium chloride solution. It is obvious that both of these systems deviate from the demanded dependency down to the lowest volume fractions used (about 1×10^{-3}). Data obtained from such first-power plots might well be misleading. While discussing such plots, it should be noted that $\frac{\ln \eta_{\text{rel}}}{\phi_v}$ should extrapolate to the same value at $\phi_v = 0$ as would η_{sp}/ϕ_v . This is because $\eta_{\text{rel}} = \eta_{\text{sp}} + 1$ and $\ln \eta_{\text{rel}} = \ln(\eta_{\text{sp}} + 1) = \eta_{\text{sp}} - 1/2 \eta_{\text{sp}}^2 + 1/3 \eta_{\text{sp}}^3 \dots$

Mark (1940) has pointed out that with elongated rods excessive viscosities will always be found even at the highest measurable dilutions; he has interpreted this fact to mean that the interaction of the disperse phase which still

exists at these dilutions goes beyond the range of validity of formulas containing only terms in the first power of concentration. The perturbations of solvent flow caused by the suspended particles are not independent, and the interaction of such perturbations can be classified into those caused by 2, 3, . . . particles by adding successive terms to a power series in volume fraction. It would seem that one must proceed to investigate the experi-

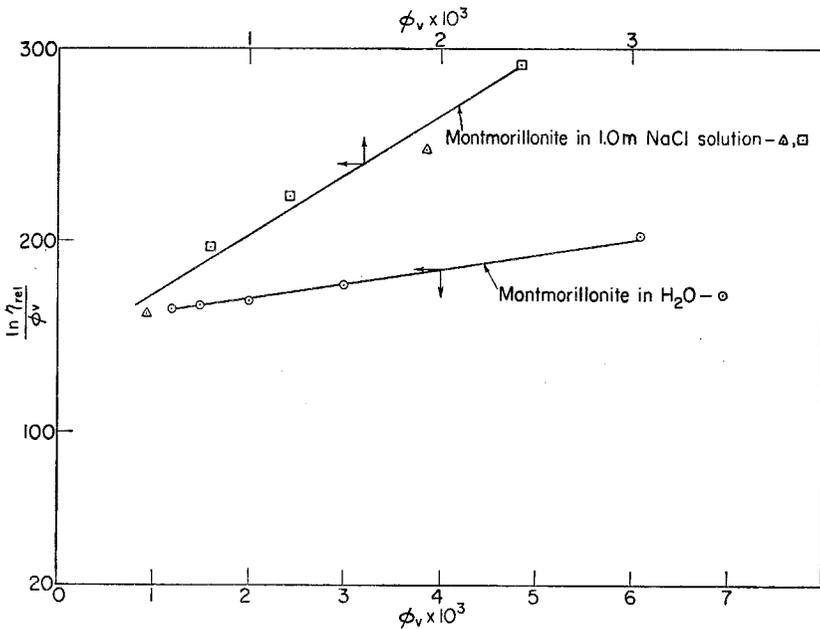


FIGURE 2.—Plot of $\frac{\ln \eta_{rel}}{\phi_v}$ vs. ϕ_v showing that functional relationship between η_{sp} and ϕ_v depends on higher powers than the first power.

mental data on the basis of higher and higher powers of volume fraction in such a power series, and here the Schulz–Blaschke equation becomes of real value. Schulz and Blaschke (1941) wrote :

$$\frac{d(\eta_{sp}/\phi_v)}{d\eta_{sp}} = k[\eta]$$

Rearranging and integrating :

$$\int d(\eta_{sp}/\phi_v) = k[\eta] \int d\eta_{sp}$$

$$\eta_{sp}/\phi_v = k[\eta] \eta_{sp} + C$$

Now, as

$$\phi_v \rightarrow 0, \eta_{sp}/\phi_v \rightarrow [\eta],$$

and since

$$\eta/\eta_0 \rightarrow 1, \eta_{sp} \rightarrow 0.$$

Therefore,

$$C = [\eta]$$

and the equation becomes

$$\eta_{sp}/\phi_v = k[\eta] \eta_{sp} + [\eta]$$

Thus, a plot of viscosity number vs. specific viscosity should yield a straight line having a slope equal to the product of the interaction index and the intrinsic viscosity or limiting viscosity number, and an intercept equal to the intrinsic viscosity. This equation can be expanded into a power series as follows :

$$\eta_{sp}/\phi_v = k[\eta] \eta_{sp} + [\eta]$$

$$\frac{\eta_{sp} - k[\eta] \eta_{sp} \phi_v}{\phi_v} = [\eta]$$

$$\frac{\eta_{sp}}{\phi_v} (1 - k[\eta] \phi_v) = [\eta]$$

or

$$\eta_{sp}/\phi_v = \frac{[\eta]}{(1 - k[\eta] \phi_v)}$$

which expands to :

$$\eta_{sp}/\phi_v = [\eta] (1 + k[\eta] \phi_v + k^2 [\eta]^2 \phi_v^2 + \dots)$$

or in an alternate form,

$$\eta_{sp} = [\eta] \phi_v + k[\eta]^2 \phi_v^2 + k^2 [\eta]^3 \phi_v^3 + \dots$$

It can therefore be seen that a plot of viscosity number against specific viscosity rather than volume fraction is a device that permits the use of a very specific type power series (i.e. coefficients are interdependent) in volume fraction, and avoids the necessity of testing higher and higher powers of concentration. Figure 3 gives data for montmorillonite in water and in 1.0 molal sodium chloride plotted by the usual technique (that is, against volume fraction) while Fig. 4 shows the Schulz-Blaschke type of plot. The improvement is obvious.

Sadron (1953) pointed out that, when ϕ_v is not infinitesimal, the quantity η_{sp}/ϕ_v becomes a function of ϕ_v which can be expressed as a power series in ϕ_v as follows :

$$\eta_{sp} = A_1 \phi_v + A_2 \phi_v^2 + \dots$$

where $A_1 = A(\rho)$, and $A(\rho)$ is a complicated function of the axial ratio developed by Simha (1940). Tables are available (see Sadron, 1953) which list the values of $A(\rho)$ arising from various values of axial ratio. A_2 is determined by the interactions, as is A_3 , etc. . . . Comparison of this approach with the expanded form of the Schulz-Blaschke equation shows that

$$\begin{aligned} A_1 &= [\eta] \\ A_2 &= k[\eta]^2 \\ A_3 &= k^2[\eta]^3 \\ &\cdot \quad \cdot \\ &\cdot \quad \cdot \\ &\cdot \quad \cdot \end{aligned}$$

This indicates that $[\eta] = A(\rho)$, and that the interaction coefficients are the products of various powers of two constant terms. The constant k is therefore a reasonable measure of the extent of particle-particle interaction, and axial ratios can be obtained from the published tables.

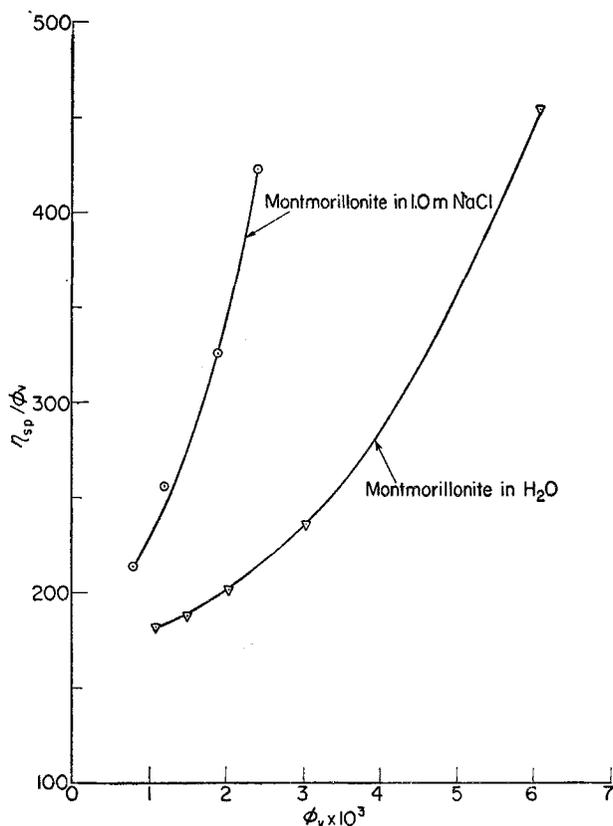


FIGURE 3.—Conventional viscosity number vs. ϕ_v plot showing uncertainty inherent in extrapolation to zero concentration.

The Kuhn equation

$$\eta_{sp}/\phi_v = 2.5 + \frac{J^2}{16}$$

expresses a much simpler functional dependence between the specific viscosity and the axial ratio, and can also be used for calculation of axial ratios for the different systems. Since this equation states [as does the Simha expression in $A(\rho)$] that specific viscosity is a constant times the volume fraction, it can only be valid for the montmorillonite-water system at infinite dilution, and the axial ratios calculated are those in which the vis-

cosity number has been replaced by the intrinsic viscosity. These axial ratios, therefore, apply only to infinite dilution. The values obtained from these calculations are collected in Table 1.

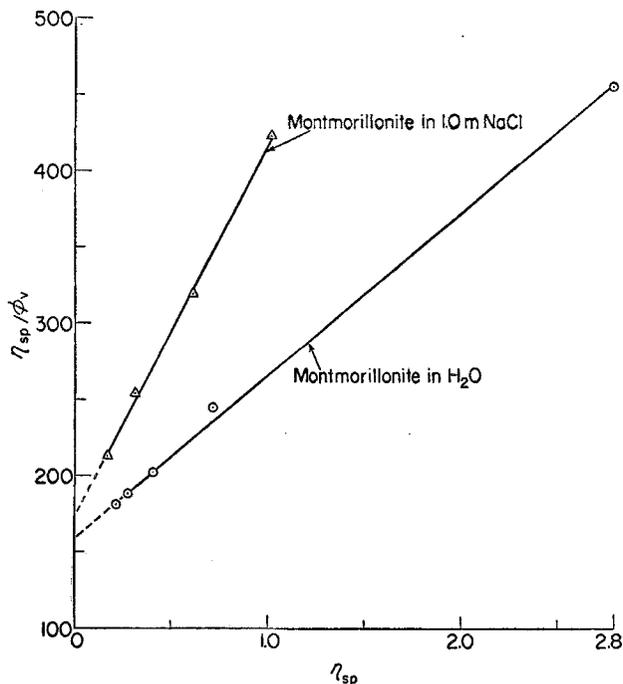


FIGURE 4.—Proposed Schulz-Blaschke plot showing improvement in ease of extrapolation to zero concentration.

TABLE 1.—CALCULATED PROPERTIES OF THE SYSTEM
MONTMORILLONITE-WATER-ELECTROLYTE

Ion	Slope = $k[\eta]$	Intercept = $[\eta]$	k	J_{Kuhn}	J_{Stmha}	Cation Hydration Energy ΔH , kcal/g-ion
None	105.8	160	0.66	50.0	47	—
Li ⁺ , 1.9 M	182.5	200	0.91	56.0	54	136
Na ⁺ , 1.9 M	224	240	0.94	61.5	60	114
K ⁺ , 1.9 M	440	188	2.34	53.2	52	94
NH ₄ ⁺ , 1.9 M	558	150	3.72	48.4	45	87
Na ⁺ , 0.5 M	142	174	0.82	52.4	48	—
Na ⁺ , 1.0 M	249	174	1.31	52.4	48	—
Na ⁺ , 2.5 M	330	135	2.4	46.0	43	—

With some exceptions, notably the discrepancy between the 1.0 M Na^+ and 1.9 M Na^+ , it is concluded that the interaction index, and thus the extent of interaction, increases with decreasing cationic heat of hydration, and increases with increasing ionic strength of added electrolyte (at constant hydration energy). It should be emphasized that the observed results

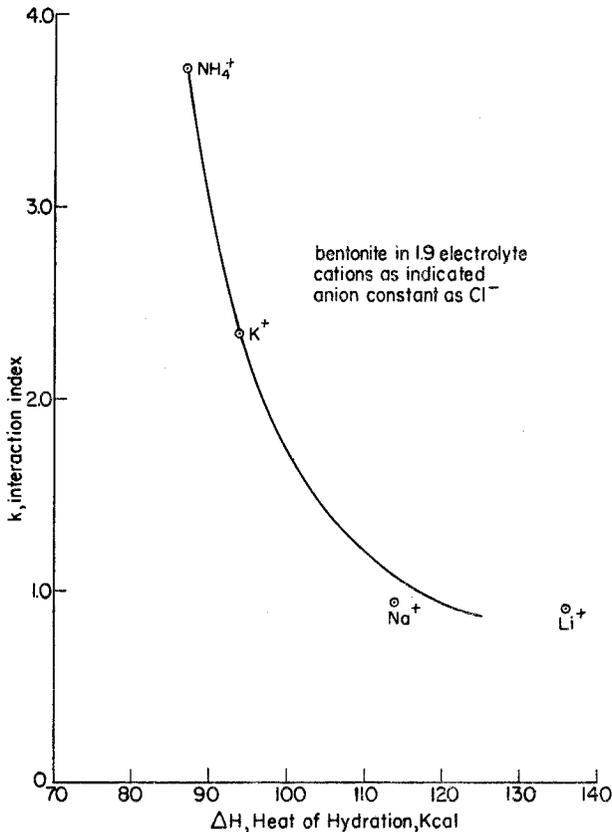


FIGURE 5.—Variation of interaction index with cationic hydration energy.

depended on the technique of preparing the samples; i.e. the electrolyte was added to the fresh-water dispersions, and no attempt was made to measure properties of direct dispersions of bentonite in electrolyte solution. Figure 5 demonstrates this variation of k with hydration energy. Table 1 also indicates the relative constancy of the axial ratio at infinite dilution.

It was of interest to determine if these results in dilute systems had any bearing on the properties of bentonite gels prepared by adding electrolyte to more concentrated fresh water dispersions. The final clay concentration

TABLE 2.—CORRELATION BETWEEN INTERACTION INDEX AND YIELD STRESS

Ion (1.9 M)	Interaction Index	Yield Stress dyn/cm ²
None	0.66	19.2
Li ⁺	0.91	134
Na ⁺	0.94	163
K ⁺	2.34	182
NH ₄ ⁺	3.72	218

was 3 percent. The gels were studied using the Fann viscometer and a correlation noted between yield stress and interaction index, as shown in Table 2 and Fig. 6.

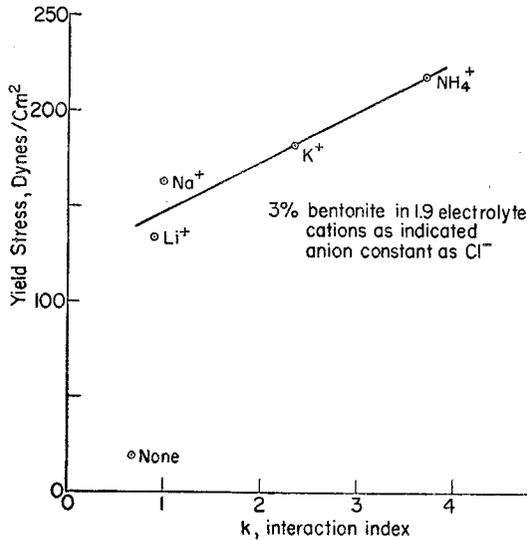


FIGURE 6.—Variation of yield stress of 3 percent gels with interaction index.

Again, the Na⁺ (1.9 M) point seems out of line and suggests that the interaction index should be considerably higher for NaCl at this concentration. Other than this point, the data seem consistent. The significant fact here is that the yield stress of 3 percent dispersions, for systems containing electrolyte, increases with increasing interaction index. Thus, a definite relationship seems to exist between the properties of the dilute dispersion and of the bentonite gels.

As was brought out earlier, the linearity of plots of η_{sp}/ϕ_v vs. η_{sp} as contrasted to the lack of linearity in the usual η_{sp}/ϕ_v plots indicates that higher powers of ϕ_v must be considered. Calculation of the contribution arising from such higher powers of ϕ_v was of interest and this has been done for the two systems appearing in Figs. 3 and 4, at two arbitrary choices of volume fraction. The results appear in Table 3. These calculations point out the importance of particle-particle interactions for a range of concentration from about 0.2 to 0.7 percent.

TABLE 3.—CONTRIBUTIONS TO η_{sp} FROM HIGHER POWERS OF VOLUME FRACTION

	ION			
	None, $k = 0.66$, $[\eta] = 160$		Na ⁺ (1.9 M), $k = 1.31$, $[\eta] = 174$	
	$\phi_v = 1 \times 10^{-3}$, $\phi_v = 3 \times 10^{-3}$		$\phi_v = 1 \times 10^{-3}$, $\phi_v = 3 \times 10^{-3}$	
$[\eta]\phi_v$	0.160	0.480	0.174	0.522
$k[\eta]^2\phi_v^2$	0.0169	0.152	0.0397	0.354
$k^2[\eta]^3\phi_v^3$	0.0018	0.0481	0.0091	0.244
$k^3[\eta]^4\phi_v^4$	—	0.0152	—	0.163

These results are in qualitative agreement with the publications mentioned earlier. Foster, Savins and Waite (1955) show much the same qualitative relationship in their study of the effect of various ions on the yield stress, and van Olphen (1956) has noted the same general relationships as in this study for the case of increasing concentration of NaCl. It should be mentioned that the electrolyte concentration employed in this work (lowest concentration = 0.5 M) corresponds to the extreme upper range of van Olphen's study. It must be emphasized that the systems employed in this and the other investigations are not strictly comparable, and such comparisons demand the use of due caution.

Another point of interest is that van Olphen found linearity in a plot of η_{rel} vs. clay concentration. Examination of the data indicated that the function $\ln \eta_{rel}/\text{conc.}$ was independent of concentration over the range of concentration presented (0.1–0.3 percent clay), as required by the idea of incremental viscosity. This paper presents data that deviate from such constancy over much the same concentration range. The difference can probably be found in the greater care used by van Olphen in the preparation of his clay samples; the behavior in the present study may be the result of traces of extraneous electrolyte. This linearity was reported for the "F suspension," containing material resulting from centrifugation of a coarser suspension, *T*, which consisted of clay of equivalent spherical radius of 2μ and less. It would be interesting to know if the same linearity was observed for the *T* suspension.

Some speculation about the reasons for the observed behavior would be

in order. The following is based largely on the publications of van Olphen (1954), Norrish (1954), M'Ewen and Pratt (1957), and M'Ewen and Mould (1957). Van Olphen has pointed out, on the basis of an ultramicroscopic counting technique, that the number of particles increases with increasing dilution, and he concludes that the number of associated layers per particle therefore varies with the clay concentration. In this connection, the values of axial ratio at infinite dilution were found to be essentially constant, regardless of electrolyte, with an average value of about 50. If the association is considered to be edge-to-edge, as seems firmly established by M'Ewen's work, this value is reasonable if one assumes rather complete dissociation at infinite dilution.

In order to account for the viscometric phenomena occurring as a function of the concentration, it seems correct to rule out face-to-face association, because such association would result in a decrease in the anisometry of the particle, or an approach to "sphericity," and such a change could not account for the rapid increase of specific viscosity with volume fraction. Here again, the most probable way to account for such concentration effects is to postulate edge-to-edge association, which would cause a rapid increase in particle anisometry with increase in concentration. This would increase viscosity due both to shape and to increased hydrodynamic interactions, involving higher powers of concentration in the power series.

Finally, something must be said about the observed effect of the extent of interaction being dependent on the particular electrolyte used. Of concern here is the fact that this dependency of interaction index with cation varies as follows: $\text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. This is the reverse of the swelling dependence noted by Norrish. Since the concentration of electrolyte was high (1.9 M), it is reasonable to consider the system as being Na^+ -bentonite in NaCl, etc. . . . The original clay sample was not homoionic but was essentially a sodium-bentonite, and the electrolytes were added to a dispersion of this clay in fresh water. If the added cation had a high hydration energy, less interaction was noted than if the opposite were true.

One explanation for this behavior is that the particle-particle equilibrium distance in the various dispersions in electrolyte solution corresponds to the minimum in the potential curve for two montmorillonite platelets in a given electrolyte. This minimum can be expected to occur at smaller values of interparticle distance as hydration energy of the cation decreases, as discussed by Norrish (1954, p. 130). Thus, the cations of low hydration energy would result in greater particle-particle interaction and higher values of the interaction index. The gel rigidity can be thought of as arising from mechanical interaction of long ribbons of particles, resulting from edge-to-edge association. This is really only a modification of the "house-of-cards" concept (van Olphen, 1954; Packter, 1957), since fewer junction points would be present, which could be counterbalanced by assuming a higher strength per junction point.

Studies in this system are being continued, with current work involving birefringence decay.

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