

Relations between particle shape, particle interaction and some rheological properties of hectorite dispersions

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The relation between viscosity and concentration of dilute aqueous hectorite (<0.2% hectorite) follows the Schulz-Blaschke equation, from which the intrinsic viscosity and particle interaction index (K) was calculated. More concentrated (up to 5.5% hectorite) dispersions possessed plastic flow properties, and a modified Schulz-Blaschke equation was used to calculate an interaction factor (\bar{K}). A correlation was established of \bar{K} and the static yield of the gels assessed by a cone and plate viscometer. The static yield value of gels was increased by the addition of sodium chloride over the range 0.001-0.005M. In the presence of 0.01M uni-univalent electrolytes the gelling power of the cations was in the order $NH_4 > K > Na > Li$. A relation between sodium chloride concentration, hectorite concentration and static yield value of the gel was derived.

The variation of specific viscosity (η_{sp}) of a suspension with volume fraction (ϕ) of spherical particles is expressed by the Einstein equation $\eta_{sp} = 2.5\phi$. This applies only to dilute suspensions of particles.

For anisotropic particles such as clay particles Packter (1956a) found the Schulz-Blaschke equation (1941) to be applicable as

$$\eta_{sp}/C = K[\eta]\eta_{sp} + [\eta] \quad \dots \quad (1)$$

where η_{sp}/C = reduced viscosity or viscosity number; $[\eta]$ = intrinsic viscosity; K = particle interaction index; C = concentration % w/v.

The equation expanded into a power series takes the form

$$\eta_{sp} = [\eta]C + K[\eta]^2C^2 + K^2[\eta]^3C^3 + \dots \quad (2)$$

For more concentrated dispersions which possess a measurable yield value, particle interaction may be represented by \bar{K} to distinguish it from interaction K , calculated from dilute dispersions. From equation (2) it can be seen that at any concentration of disperse phase

$$\bar{K} = \eta_{sp} - [\eta]C \quad \dots \quad (3)$$

will measure the contribution of particle interaction to the specific viscosity. This modified equation was deduced by Packter (1956b). By applying the Schulz-Blaschke equation to montmorillonite-water dispersions Packter (1956a,b) and Granquist (1959) obtained data showing the effect of factors such as particle interaction, immobilization of dispersing medium, particle size and shape, formation of aggregates and the presence of electrolytes on the flow properties of the systems.

In the present work the Schulz-Blaschke equation has been applied to dilute (<0.2% w/v) dispersions of a synthetic hectorite to calculate interaction index (K) and intrinsic viscosity. The equation as modified by Packter (1956b) was used to study higher concentrations (i.e. > 1% w/v) which exhibited plastic flow behaviour. The aim was to seek relations between intrinsic viscosity and interaction index concentrated dispersions.

MATERIALS AND METHODS

Materials

Hectorite: Laponite CP, a synthetic hectorite supplied by Laporte Industries Limited. The chemical and physical properties have been reported by Neumann (1970).

Distilled water—triple glass-distilled water; conductivity $1.72 \mu\text{mhos cm}^{-1}$.

Electrolytes—ammonium chloride, sodium chloride, potassium chloride—analytical reagent quality. Lithium chloride—laboratory reagent quality (BDH).

Apparatus

Suspended level glass capillary viscometer: efflux time of water at $30^\circ = 163.4$ s.

Cone-plate viscometer—the Ferranti Shirley cone-plate viscometer with automatic program unit and X-Y recorder was used (McKenna, 1954, 1956). The viscometer was calibrated with silicone fluid 1.9P and inertial effects of the cone were absent when a sweep time of 60 s was used. In the determination of static yield value, inertial effects are considered to be negligible. It was fitted with a 7 cm cone (angle 0.3°) and a 600 g torque spring. A vapour hood designed to prevent loss of moisture from samples was used as described by Chawla (1967).

Preparation of dispersions

Dispersions were prepared by weighing hectorite powder into water at room temperature and stirring at a high speed with a Silversen mixer for 10–15 min. When a dispersion containing an electrolyte was required, a concentrated solution of the electrolyte was added to the dispersion just before mixing was completed. All dispersions were aged for 24 h before being used.

Relative viscosity

The relative viscosity of dispersions containing up to 0.18% w/v hectorite in water or electrolyte solution at $30^\circ \pm 0.01^\circ$ was determined using the suspended level viscometer.

Static yield value

For hectorite dispersions possessing a measurable yield value, the rate of shear versus shear stress curves were determined with the cone-plate viscometer fitted with an X-Y recorder. 60 s sweep time was used and temperature maintained at $30^\circ \pm 0.05^\circ$. Each sample was subjected to a standard preliminary treatment which consisted of leaving the sample between the cone and plate for 2 min to attain temperature equilibrium, shearing for 2 min (60 s up; 60 s down) and leaving for another 3 min. This was done to overcome changes in rheological properties due to sample disturbance while transferring from the container to the viscometer plate and during subsequent raising of the plate to the operational position. The static yield value was estimated from the spur value of the flow curve (Fig. 1).

RESULTS AND DISCUSSION

For dispersions containing less than 0.2% w/v hectorite the data were treated according to equation (1) reduced viscosity being plotted against specific viscosity to obtain a straight line with a slope equal to $K[\eta]$ (Fig. 2). Values of intrinsic viscosity and interaction index (K) for dispersions in solutions of sodium chloride, potassium

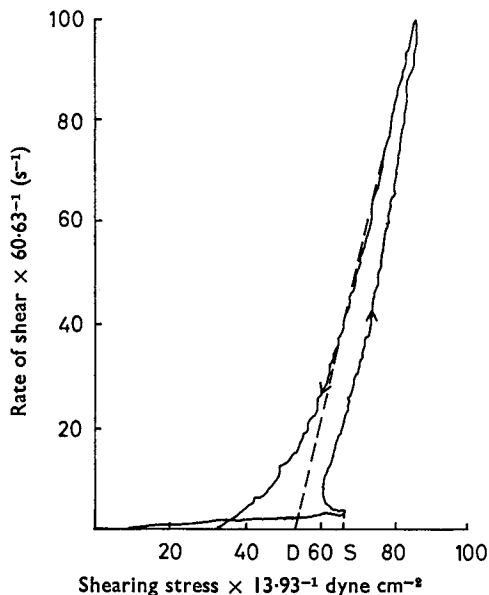


FIG. 1. Flow curve for 4% w/v hectorite in 0.001M NaCl (cone and plate viscometer). Gel aged 24 h. S = static yield value. D = dynamic yield value.

chloride and lithium chloride are given in Table 1. This Table shows that intrinsic viscosity and interaction index increased with the rise in concentration of electrolyte and that at a particular electrolyte concentration interaction index was highest for dispersions in potassium chloride solutions and lowest for those in lithium chloride solution. Values of hydration energy shown in the table were taken from Norrish (1954) who suggested that the dependence of particle interaction on cation may be due to the differences in hydration energy of K^+ , Na^+ and Li^+ . Norrish (1954) has suggested that the equilibrium distance between particles dispersed in electrolyte solution may correspond to the minimum in the potential energy versus distance curve for two particles. Probably as hydration energy of the cation decreases, the interparticle distance at which the minimum occurs in the potential curve decreases. Thus the average distance between the particles would be least in the presence of potassium, hence the highest values of interaction index.

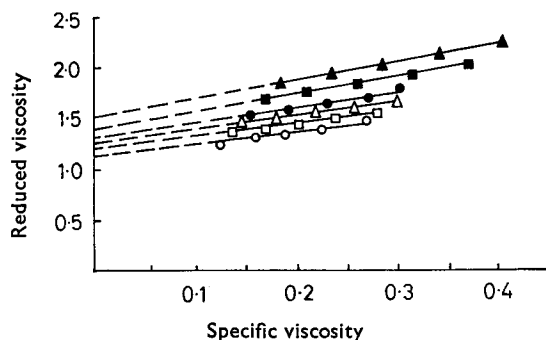


FIG. 2. Reduced viscosity against specific viscosity of hectorite dispersion for the determination of intrinsic viscosity and interaction index. (K) \circ Water; \circ 0.001M NaCl; \triangle 0.002M NaCl; \bullet 0.003M NaCl; \blacksquare 0.004M NaCl; \blacktriangle 0.005M NaCl.

Dispersions of hectorite ($>4\%$ w/v in water or $>3\%$ in electrolyte solution) exhibited thixotropy and a typical flow curve is shown in Fig. 1. The reciprocal of the slope of the linear portion of the down-curve is the plastic viscosity, η_{pl} . Table 2 shows the particle interaction values (\bar{K}) calculated using equation (3) and η_{sp} calculated from η_{pl} values.

Fig. 3 shows that for gels containing from 3 to 5.5% hectorite dispersed in sodium chloride there is a linear relation between \bar{K} and static yield value S . The relation between K and S at any particular sodium chloride concentration can be represented by the equation

$$\bar{K} = PS + q \quad \dots \dots \dots (4)$$

where P is the slope of the line obtained by plotting \bar{K} against S and q the intercept (Fig. 3). The slope P varied with the concentration of electrolyte but the intercept q was found to be constant. This is in contrast to Packter's (1956b) finding of a direct relation between \bar{K} and S , that is, $\bar{K} = PS$. However, it shows that in hectorite dispersions particle interaction is always present to some extent even if the system does not give a measurable yield value. Electrolyte-free dispersions containing 3% or less of hectorite could not be studied since the yield value was below the level of detection. Prolonged ageing (48 h or more) gave a gel with a measurable yield value but the plastic viscosity was too small for a meaningful value of \bar{K} to be calculated.

Neumann (1956) has reported from electron microscopic studies that hectorite consists of needle-like plates with some primary particles as small as 0.6–1.5 nm in width and 10–20 nm in length. The highly anisometric shape of hectorite particles together with the swelling which occurs in water are probably the cause of the departure from the viscosity-concentration relation given by Einstein's equation, hence the need to use the Schulz-Blaschke equation.

The high intrinsic viscosity of hectorite in water, 115 compared with 2.5 for Einstein's system of spheres may also be attributed to the shape of the particles. Simha(1940)

Table 1. *Variation of intrinsic viscosity and interaction index with uni-univalent electrolyte concentration and with cation.*

Dispersing medium	Intrinsic viscosity $[\eta]$	Interaction index K	ΔH
Water	1.150	0.892	
0.001M NaCl	1.225	0.949	
0.002	1.275	1.069	
0.003	1.325	1.114	114
0.004	1.400	1.214	
0.005	1.525	1.287	
0.001M KCl	0.950	1.074	
0.003	1.075	1.329	
0.005	1.225	1.536	94
0.001M LiCl	1.100	0.902	
0.003	1.225	0.993	136
0.005	1.350	1.181	

ΔH = Cation hydration energy k cal/g ion (values calculated by Norrish, 1954).

$[\eta]$ = 0.025 in Einstein equation when concentration of disperse phase expressed as % v/v.

Table 2. Yield value, plastic viscosity, specific viscosity, intrinsic viscosity and interaction index of hectorite dispersions.

Dispersing medium	Hectorite concentration (% w/v)	Static yield value (dyne cm ⁻²)	Plastic viscosity (poise)	Specific viscosity	Intrinsic viscosity [η]	Interaction index \bar{K}
Water	C	S	η_{p1}	η_{sp}	1.150	\bar{K}
	4.0	497	0.573	70.5		65.9
	4.5	709	0.779	96.3		91.1
	5.0	966	0.992	122.9		117.2
	5.5	1192	1.201	149.0		142.7
0.001M NaCl	3.0	144	0.248	30.7	1.225	27.1
	4.0	589	0.547	73.3		70.4
	5.0	1122	1.030	130.7		124.6
0.002M NaCl	3.0	215	0.267	33.1	1.275	29.3
	4.0	695	0.627	79.1		74.0
	5.0	1271	1.037	131.5		125.2
0.003M NaCl	3.0	263	0.304	37.9	1.325	33.9
	4.0	788	0.647	81.7		76.4
	5.0	1463	0.074	136.1		129.5
0.004M NaCl	3.0	331	0.330	41.1	1.400	37.0
	4.0	950	0.687	86.7		81.1
	5.0	1634	1.103	139.9		132.9
0.005M NaCl	3.0	426	0.361	45.2	1.525	40.6
	4.0	1082	0.714	90.3		84.2
	5.0	1841	1.131	143.5		135.9

$\eta_{sp} = (\eta_{p1}/\text{viscosity of dispersing medium}) - 1$.

has shown that as particles become less isometric intrinsic viscosity increases. Application of Kuhn's (1933) equation relating intrinsic viscosity [η] and particle shape

$$[\eta] = 2.5 + \frac{J^2}{16} \dots \dots \dots (5)$$

where J is the axial ratio, gives 42.4 as the average axial ratio of hectorite particles confirming the anisometric shape reported by Neumann (1965).

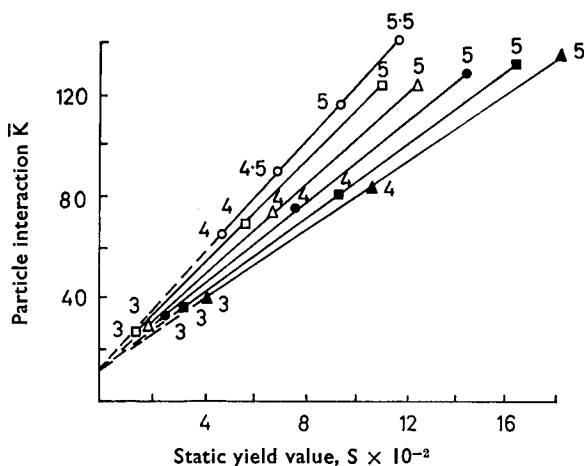


FIG. 3. Relation between particle interaction (\bar{K}) and static yield value (S) of hectorite gels. ○ Water; 0.001 M NaCl; △ 0.002M NaCl; ● 0.003M NaCl; ■ 0.004M NaCl; ▲ 0.005M NaCl. Numbers on graph represent concentration of hectorite (% w/v).

Increasing the concentration of sodium chloride in aqueous hectorite dispersions from 0.0–0.005M caused the intrinsic viscosity to rise from 1.501 to 1.525. This is an indication of increasing anisometry of the dispersed particles as more electrolyte was added to the system and may be explained in terms of the various ways in which particles could associate during flocculation. Of the three possible types of particle-particle association, edge-to-edge, edge-to-face, and face-to-face, the first two would lead to increased anisometry and are therefore, probably responsible for the rise in intrinsic viscosity. Face-to-face association would produce thicker and less anisometric particles which would have caused the intrinsic viscosity to fall.

Particle interaction index (K) of dilute dispersions depends on both the concentration of electrolyte and the cation as shown in Table 1 and it was of interest to determine how changes brought about by altering the electrolyte or the cation were related to static yield value (S). Fig 4A and B are plots of static yield value versus interaction index. In Fig. 4A the interaction index was increased by raising the concentration of electrolyte; in Fig. 4B a similar effect was achieved by altering the cation. These figures suggest that there is a definite relation between interaction of particle in dilute suspensions and the yield value of concentrated dispersions.

Using clays of different particle shape Packter (1956b) showed that the slope of \bar{K} versus S plot (equation 4) decreased as the particles became more anisometric. As the concentration of sodium chloride in the dispersions was raised in 0.001 increments from 0.001 to 0.005 the slope of the \bar{K} versus S plot decreased from 0.133 to 0.078 which is consistent with increasing anisometry (Table 3). This is in agreement with results obtained from dilute dispersions where intrinsic viscosity, taken as an indication of particle anisometry was found to increase with electrolyte concentration. The principal factors that will determine the static yield value of a hectorite dispersion are its concentration, the concentration of electrolyte and the nature of electrolyte. A relation between these factors was derived as follows:

The relation between particle interaction \bar{K} and concentration of sodium chloride

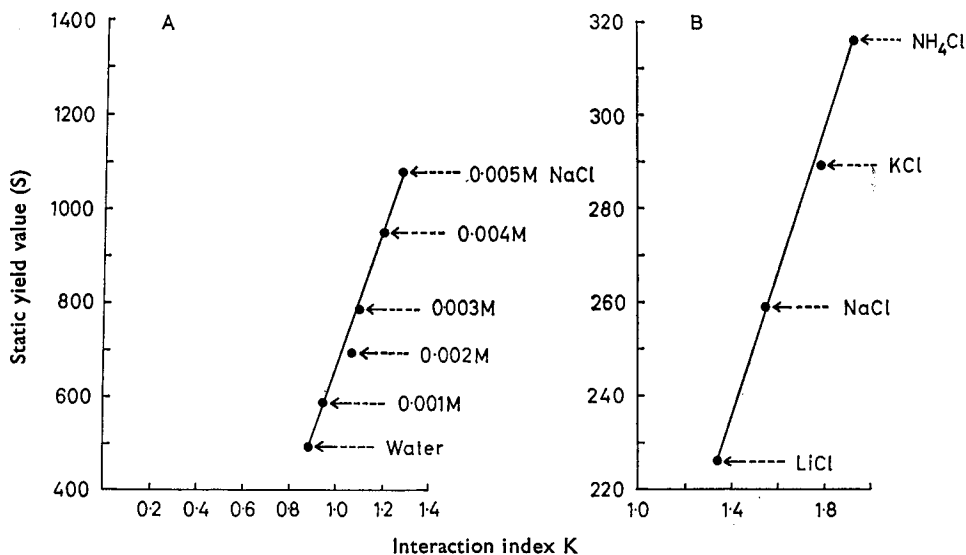


FIG. 4. Relation between static yield value (S) of 4% hectorite gel and interaction index (K) in dispersions containing (A) varying amounts of sodium chloride and (B) containing 0.01M univalent electrolytes.

for gels containing the same amount of hectorite is shown in Fig. 5. This may be represented by the equation

$$\bar{K} = ma + b \quad \dots \quad \dots \quad \dots \quad (6)$$

where a = molar concentration of electrolyte; m = slope; b = intercept on K axis. For the data in Fig. 5 the equation can be stated

$$\bar{K} = 3500a + 44(C - 2.5) \quad \dots \quad \dots \quad \dots \quad (7)$$

where C is the concentration (% w/v) hectorite

If equation (4) is modified to include the effect of sodium chloride:

$$\bar{K} = fPS + q \quad \dots \quad \dots \quad \dots \quad (8)$$

where f is a function of the sodium chloride concentration, equations (7) and (8) can be combined to give

$$S = \frac{3500a + 44(C - 2.5) - q}{M_1^{(0.96)r}} \quad \dots \quad \dots \quad \dots \quad (9)$$

where $M_1 = 11$ = slope of \bar{K} vs S in absence of electrolyte; $q = 13$ = intercept on \bar{K} vs S plot; $r = (\text{molar concentration of NaCl}/0.001) + 1$.

Equation (9) relates the yield value S to the concentration of hectorite (3–5%) and sodium chloride (0.001 to 0.005M).

The experimentally determined values of S are compared with those calculated from equation (9) in Table 4. More experimental data are required to verify the applicability of this equation to a wider range of hectorite and electrolyte concentrations but in its present form it gives an estimate of yield values up to 17×10^2 dyne cm^{-2} . The lowest yield value measured in this present work was 1.44×10^2 dyne cm^{-2} and was limited by the sensitivity of the cone and plate viscometer.

Sufficient concentration of hectorite in an aqueous dispersing medium leads to the formation of a continuous structure throughout the system (gel) making it suitable as a vehicle for suspending dispersed solids. The ability of the gel to suspend dis-

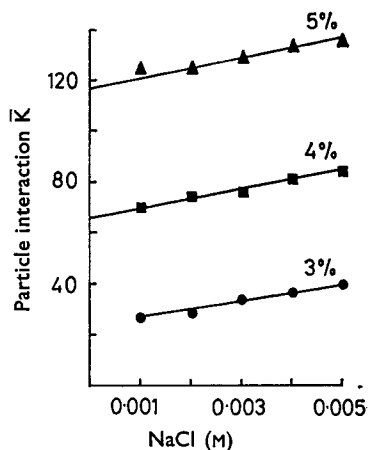


FIG. 5. Relation between particle interaction (\bar{K}) and concentration of sodium chloride. ● 3%; ■ 4%; ▲ 5% w/v hectorite.

Table 3. *Variation of particle shape with electrolyte concentration.*

NaCl (concentration molar)	Slope of \bar{K} versus S plot
None	0.133
0.001	0.119
0.002	0.106
0.003	0.096
0.004	0.085
0.005	0.078

Table 4. *Yield values of Hectorite gels—comparison of calculated and experimentally determined values.*

Hectorite concentration (% w/v)	NaCl concentration (M)	Static yield values dyne cm ⁻²	
		Experimental	Calculated
5	0.001	1122	1104
	0.002	1271	1247
	0.003	1463	1469
	0.004	1634	1558
	0.005	1841	1753
4	0.001	589	620
	0.002	695	720
	0.003	788	868
	0.004	950	949
	0.005	1082	1080
3	0.001	144	137
	0.002	215	192
	0.003	263	267
	0.004	331	326
	0.005	426	406

persed solids would be determined by the strength of the structure measured by the static yield value. The relation between yield value and the size of particle that will remain in permanent suspension is reported by Carless & Ocran (1972).

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