DIVISION S-9—SOIL MINERALOGY

Rheological Properties of Aqueous Suspensions of Palygorskite

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ABSTRACT

The rheology of aqueous suspensions of six palygorskites with different particle morphologies has been investigated as a function of clay concentration, adsorbed ion, pH, and electrolyte concentration, using a rotary viscometer. Rheological parameters (plastic viscosity, Bingham yield value, and apparent viscosity) increase with the length/width ratio of individual palygorskite fibers. The plastic viscosity increases linearly with clay concentration within the range investigated (up to 5% w/v). The rheological parameters are higher for clays saturated with divalent ions than those for clays saturated with monovalent ions. For ions of the same valency the rheological parameters tend to increase with decreasing radius of the hydrated ion. The flow of suspensions is pseudoplastic regardless of the nature of the adsorbed ion. Measurements of electrophoretic mobility in very dilute suspensions suggest that the point of zero charge of the palygorskite surface is at pH 4 to 4.5. Scanning electron microscopy indicates significant differences in fiber arrangement between low and high pH values. Face-to-face particle association occurs at low pH values, giving rise to close-packed domains of fibers, while at high pH values the fibers adopt a random orientation. The flow of suspensions is pseudoplastic at pH $\leq$ 7 and changes to Newtonian at pH $\geq$ 9. At pH $\leq$ 7 the rheological parameters remain relatively constant even at high electrolyte concentrations, but at pH $\geq$ 9 they are influenced significantly by electrolyte addition. Electrolyte-free palygorskite suspensions at pH 7 are antithixotropic. When the pH falls below 7 or when electrolyte is added, the suspensions coagulate and become thixotropic. Some rheological properties of palygorskite are similar to those of platy clay minerals such as kaolinite and montmorillonite, while other rheological properties deviate considerably. The models developed to explain the rheological behavior of platy clay minerals do not always account for the behavior of palygorskite, because of differences in particle morphology and surface structure.

S OME SOILS in arid and semiarid areas contain palygorskite in their clay fraction. Palygorskite is a so called "special clay", characterized by a microfibrous morphology and a relatively low surface charge. The effect of the common clay minerals, such as smectite, kaolinite, and illite, on the properties of soils has been studied and is known in great detail (e.g., Dixon and Weed, 1989). However, with regards to palygorskite, no information of this nature is available. This constitutes a serious impediment for the proper management of these soils. Nearly all palygorskite-containing soils are found in dry areas, where irrigation is indispensable for profitable agriculture. For proper irrigation practices, the

physical behavior of wetted soils is of paramount importance.

When the electrolyte concentration in the percolating solution in soil is below the flocculation value of the clay, clay dispersion occurs. Under such conditions water flow in the soil changes from flow of solution to flow of clay suspension (Pupisky and Shainberg, 1979). The presence of clay particles in the percolating solution may increase significantly the viscosity of the flowing suspension and therefore may affect the hydraulic conductivity of the soils, which is important for the management of irrigation. The suspension viscosity increases even further when particle–particle interactions occur.

The rheological parameters of clay suspension can be used to evaluate particle–particle interactions. The model of edge-to-face particle association was first proposed by Hofmann and Hausdorf (1945). The concept of face-to-face, edge-to-face, and edge-to-edge type associations in suspension of platy clay minerals (such as montmorillonite and kaolinite) was developed further by van Olphen (1977). These simple models of particle–particle interactions have been helpful for understanding the stability and rheological behavior of clay–water systems.

Several studies have been devoted to the rheological properties of montmorillonite and kaolinite suspensions (Heath and Tadros, 1983; Brandenburg and Lagaly, 1988; Lagaly, 1989; Permien and Lagaly, 1994, 1995; Keren, 1988, 1989, 1991), which are found to be influenced by the size and shape of particles, clay concentration, nature of the exchangeable ion, pH, and electrolyte concentration.

Palygorskite has a wide range of industrial applications because of its special sorptive, colloidal-rheological, and catalytic properties, one of which is its usage as drilling muds. Palygorskite muds have the advantage over other clays (such as smectite) in being less sensitive to salts; that is, the desired rheological properties remain virtually constant even at high electrolyte concentrations (Galan, 1996).

The rheological properties of a palygorskite clay from Ukraine (Ovcharenko, 1963), Florida (Kheng, 1989), and Central Spain (Galan et al., 1994) have been investigated more from the perspective of their application than in terms of particle–particle interactions. Moreover, the samples used contained impurities of phyllosilicates (smectite for the clay from Florida, smectite and illite for the clay from Ukraine and Central Spain) and other minerals (quartz, calcite). These impurities can

Abbreviations: EM, electrophoretic mobility; MB, Methylene Blue; PZC, point of zero charge.

strongly affect the rheological behavior of suspensions. We know of no references on the rheological properties of pure palygorskite.

In addition, the question arises whether the models of particle–particle interactions that van Olphen (1977) has suggested for suspensions of platy clay minerals are applicable to palygorskite. To this end, we have investigated rheological properties of aqueous suspensions of palygorskites with different morphology as a function of clay concentration, nature of adsorbed ion, pH, and ionic strength.

MATERIALS AND METHODS

Palygorskites

Six palygorskites were used: Mt. Flinders (Queensland, Australia), Mt. Grainger (South Australia), Florida and Georgia (USA), Yucatan (Sacalum, Mexico), and Negev (Israel). Florida palygorskite (PFl-1, Gadsden County) was obtained from the Source Clay Minerals Repository (Columbia, MO); the others were obtained from independent sources.

The natural clays were ultrasonically dispersed in water and the <2-mm fraction was separated by sedimentation under gravity. The clays were then lightly treated with 0.1 M HCl for the removal of carbonates. The sample from Mt. Grainger contained considerable amounts of free iron oxides, which were extracted by dithionite–citrate–bicarbonate method (Klute, 1986). Clays saturated with Li, Na, Mg, Ca, or Ba were prepared by treating the clay-size fraction three times with 1 M solution of a chloride salt with the respective cation, washing with distilled water, and centrifuging until the electrical conductivity of the equilibrium solution was <1 S m^{-1}. The clays were then freeze-dried.

X-Ray Diffraction

X-ray diffraction data were obtained with a Rigaku diffractometer with Cu Kα radiation. Oriented slides of Ca-saturated clays were prepared and solvated with ethylene glycol vapor (65°C for 24 h). The samples from Mt. Flinders, Mt. Grainger, Yucatan, and Negev were remarkably free of other aluminosilicates. However, the samples from Florida and Georgia contained small amounts of smectite.

The amounts of smectite in Florida and Georgia samples were quantified using binary montmorillonite–palygorskite mixtures as external standards (Brindley, 1980). The intensity of x-ray diffraction by a component in the mixture depends on, among other factors, chemical composition of the component (Brindley, 1980). The chemical composition of the Yucatan sample was very close to that of the Florida and Georgia samples (Neaman and Singer, 2000). For this reason, the Yucatan sample was chosen as an external standard.

Mixtures of Ca-saturated palygorskite from Yucatan and montmorillonite from Wyoming (SWy-1, Crook County) containing 5, 10, and 15% (w/w) of montmorillonite were prepared. Oriented clay slides were prepared and solvated with ethylene glycol vapor (65°C for 24 h). The x-ray diffraction peak intensities were measured for smectite (001) and palygorskite (110) in prepared Yucatan–Wyoming mixtures and the Florida and Georgia samples. A calibration curve was obtained by plotting the smectite/palygorskite intensity ratio vs. smectite/palygorskite weight ratio in the prepared mixtures. From this calibration, the smectite/palygorskite weight ratio in the Florida and Georgia samples was calculated. Florida and Georgia samples contain 2.8 and 3.1% (w/w) of smectite, respectively.
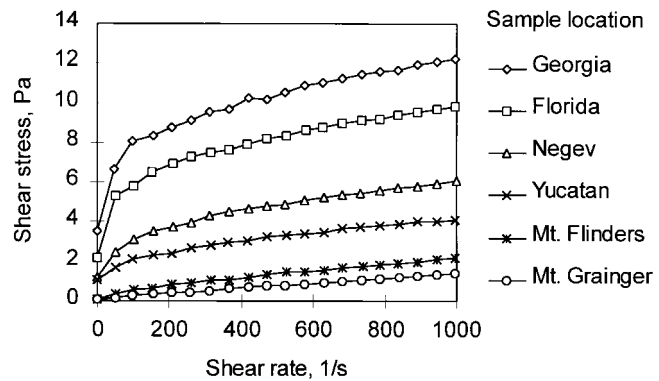

Fig. 1. Flow curves of 3% (w/v) suspensions of Na–palygorskites at pH 7.

Rheological Measurements

Rheological properties of aqueous suspensions were determined at 25°C with a Haake viscometer (model CV 20, Karlsruhe, Germany) of the Couette type with a rotating outer cylinder and a stationary inner cylinder. The gap between the two cylinders was 0.32 mm (sensor system ZB 30). Freeze-dried palygorskite samples were dispersed in water or 0.001, 0.01, and 0.1 M NaCl solutions, and ultrasonified to obtain homogeneous suspensions. For studies on pH-dependence, the pH of the suspensions was adjusted by addition of dilute HCl or NaOH. The samples were shaken for 1 h, and the pH was adjusted several times until the required pH was obtained. Samples were shaken for 24 h before rheological measurements were started. Rheological measurements were carried out in duplicate.

Studies of time-dependent phenomena (thixotropy and rheopexy) of the Florida sample were carried out with a high degree of accuracy using a Physica rheometer (model UDS 200, Physica, Stuttgart, Germany).

Electrophoretic Mobility Measurements

Electrophoretic mobility (EM) was measured by electrophoresis of very dilute suspensions using a Lazer Zee meter (model 501, Pen Kem, New York). Average EM of 200 to 500 individual particles was calculated by the instrument. The clays were dispersed by ultrasonication in water or NaCl solution. The pH of suspensions was adjusted by addition of dilute HCl or NaOH and measured with fine-step color indicators.

Electron Microscopy

Electron microscopy examinations were carried out using a scanning electron microscope (JSM-5410LV, JEOL, Tokyo, Japan) and a transmission electron microscope (JEM-100CX, JEOL). For studies of the effect of pH on particle arrangement, the suspensions of palygorskite at different pH values were allowed to settle onto scanning electron microscope stubs and frozen immediately. After that, the drop on the stub was freeze-dried. It was assumed that freeze-drying does not alter the original arrangement of the palygorskite fibers in suspension.

RESULTS AND DISCUSSION

Effect of Fiber Morphology

Figure 1 shows plots of shear rate against shear stress of 3% (w/v) suspensions of Na–palygorskites at pH 7. The Mt. Grainger and Mt. Flinders palygorskites exhibit

Table 1. Plastic viscosity, Bingham yield value, and apparent viscosity of palygorskite suspensions at pH 7.

	3% (w/v) Adsorbed ion			5% (w/v) Adsorbed ion		
Sample	Na^+	Mg^{2+}	Ca^{2+}	Na^+	Mg^{2+}	Ca^{2+}
	Plastic viscosity, mPa s					
Mt. Grainger	1.29	1.45	1.40	1.54	1.90	1.90
Mt. Flinders	1.71	1.86	1.80	2.78	3.04	3.07
Yucatan	1.93	4.20	3.47	3.72	10.31	8.94
Negev	2.63	2.73	2.67	4.91	4.98	4.96
Florida	3.54	5.57	5.11	7.05	10.33	9.84
Georgia	4.11	7.01	6.21	7.92	12.48	10.18
	Bingham yield value, Pa					
Mt. Grainger	0.13	0.19	0.13	0.14	0.17	0.15
Mt. Flinders	0.49	0.73	0.85	1.89	2.23	2.43
Yucatan	2.27	6.39	6.59	13.06	16.24	18.65
Negev	3.50	4.12	3.93	10.32	11.45	11.26
Florida	6.44	7.44	7.26	15.89	17.85	19.30
Georgia	8.32	9.61	8.63	16.39	17.40	18.64
	Apparent viscosity at shear rate 1000 s^{-1}, mPa s					
Mt. Grainger	1.39	1.63	1.53	1.64	2.02	2.02
Mt. Flinders	2.18	2.55	2.62	4.61	5.20	5.40
Yucatan	4.12	10.43	9.88	16.63	26.16	27.16
Negev	6.06	6.76	6.55	16.18	16.25	16.20
Florida	9.89	12.86	12.30	22.57	27.79	28.73
Georgia	12.29	16.48	14.68	23.97	29.67	28.76

Table 2. Length (*L*), width (*W*), and ellipticity (*L/W*) of palygorskite fibers.

Sample	*L*	SD	*W*	SD	*L/W*	SD
	nm		nm			
Mt. Grainger	375	99	37	9	10.1	2.8
Mt. Flinders	562	129	34	8	17.3	4.2
Yucatan	816	233	29	7	26.8	7.3
Negev	1260	343	37	9	33.7	9.7
Florida	921	168	32	7	29.7	7.8
Georgia	613	153	26	7	23.8	6.6

a nearly Newtonian flow. For all other palygorskite samples the flow curves are typical of clay materials with a pseudoplastic behavior (van Olphen, 1977). At low rates of shear, such systems exhibit non-Newtonian flow, which is characterized by a progressive decline in viscosity as shear rate increases. Above a certain value of shear rate, the flow curve becomes linear.

Pseudoplastic flow of colloid suspensions can be described by the Bingham model (Güven, 1992a). According to this model the slope of the linear part of the flow curve is referred to as the plastic viscosity, and the intercept of the linear portion of the curve with the stress axis is referred to as the Bingham yield (stress) value. For all samples the flow curves become linear at shearing rates of 250 to 1000 s^{-1}. Another rheological parameter is the apparent viscosity, which is defined as shear stress/shear rate ratio at any shear rate. In our study the apparent viscosity was obtained at a shear rate of 1000 s^{-1}. Values of plastic viscosity, Bingham yield, and apparent viscosity are shown in Table 1.

As discussed below, the individual fibers of palygorskite are associated into microaggregates. The microaggregates progressively break down as the rate of shear increases, leading to an overall decrease in viscosity. There is a certain shear rate at which structural disruption is complete, and above which the viscosity remains constant. Viscosity is a measure of the resistance to flow of individual fibers of palygorskite, while yield stress represents the work required to break down the microaggregates.

It is suggested that differences in flow curves between samples are related to the size and shape of individual palygorskite fibers. The size and shape of individual particles were determined by transmission electron microscopy in order to confirm the hypothesis. The length (*L*) and width (*W*) of the fibers were measured using a computer program, and the *L/W* ratio was calculated (Table 2). The results indicate that the samples differ

from each other in the length of the fibers, while the width of the fibers is practically the same for all samples. Figure 2 shows transmission electron micrographs of the Yucatan and Mt. Flinders samples. The former clay is characterized by relatively long fibers, and the latter sample consists of relatively short ones.

The first theoretical deviation of the viscosity of suspensions was obtained by Einstein (1906). He showed that for a suspension of glass spheres of colloidal dimensions:

$$\eta_r = 1 + k\varnothing$$

where η_r represents relative viscosity and $\varnothing$ represents the volume fraction of the particles in the suspension. For spheres, the coefficient k equals 2.5. According to Güven (1992a), the nonspherical forms are described as ellipsoids, and the coefficient k is correlated with the ellipticity of the particles. The ellipticity of fibers is

Fig. 2. Transmission electron micrographs of the (a) Yucatan and (b) Mt. Flinders samples.
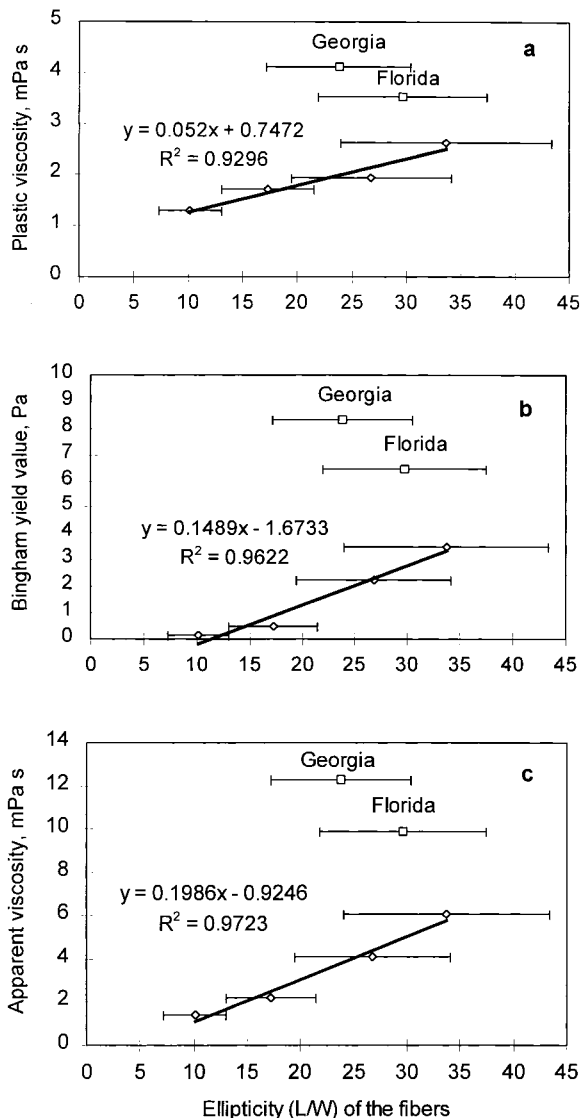
Fig. 3. Effect of fiber ellipticity on (a) plastic viscosity, (b) Bingham yield value, and (c) apparent viscosity of 3% (w/v) suspensions at pH 7 for Na–palygorskites used in the study.

Fig. 4. Flow curves of Na–palygorskite from the Negev at different suspension concentrations at pH 7.

required for orientation, increases with the ellipticity of the particles. The high correlation of ellipticity with plastic and apparent viscosities (Fig. 3a and 3c, respectively) provide further support for this postulate. Similar correlations were reported by Kahn (1959) for montmorillonite, illite, hectorite, nontronite, and palygorskite suspensions.

The ellipticity of the fibers is also related to the Bingham yield value (Fig. 3b). As discussed below, individual fibers of palygorskite in suspension are associated to each other by faces. The intimacy of association would increase with fiber length due to an increase in the area of the contact. Thus, the Bingham yield value of the suspensions increases with fiber ellipticity.

Effect of Clay Concentration

Figure 4 shows the flow curves of Na–palygorskite from the Negev at different suspension concentrations. The suspensions exhibit nearly Newtonian flow at a concentration of 1% (w/v), but the flow becomes pseudoplastic as suspension concentration increases. Analogous results were obtained for Na–montmorillonite suspensions, which exhibited Newtonian flow at a suspension concentration of 1% (w/v) (Shainberg and Otoh, 1968) and pseudoplastic flow at a suspension concentration of 2.5% (w/v) (Keren, 1988). The increase in the Bingham yield value with clay concentration is due to the increase of number of clay particles in the suspension. The threshold value of shear rate at which flow changes from non-Newtonian to linear also depends on suspension concentration.

Plastic viscosity of Na–palygorskite suspensions of all samples increased linearly with increasing clay concentration within the range investigated (Fig. 5). Correlation coefficients (R^2) between plastic viscosity and suspension concentration were higher than 0.9 for all samples. All lines converge to a viscosity of 0.89 mPa s when extrapolated to zero concentration. This value equals the viscosity of water at 25°C, the suspending medium used in this study.

Keren (1989) reported a Bingham yield value of 3.6 Pa for a 2.5% (w/v) suspension of Na–montmorillonite from Wyoming at pH 7, and an apparent viscosity of 5.6 mPa s. For the Mt. Grainger and Mt. Flinders samples, these values are much lower than those for Wyo-

defined as L/W ratio where L is the length and W is the width of the fibers.

The effect of ellipticity of the fibers on plastic viscosity, Bingham yield value, and apparent viscosity of 3% (w/v) suspensions of Na–palygorskites is shown in Fig. 3. Similar relationships between ellipticity and rheological parameters were obtained for 5% (w/v) suspensions (not shown). Figure 3 shows that for the Mt. Grainger, Mt. Flinders, Yucatan, and Negev palygorskites all rheological parameters are linearly related to the ellipticity of the fibers. However, the plastic viscosity, Bingham yield value, and apparent viscosity of the Georgia and Florida clay suspensions are much higher than would be predicted from the observed relationships because of the presence of smectite impurities.

According to Güven (1992a), ellipsoids are oriented during the flow with respect to the flow direction, increasing the amount of dissipated energy and, hence, the viscosity of the fluid. The amount of dissipated energy,
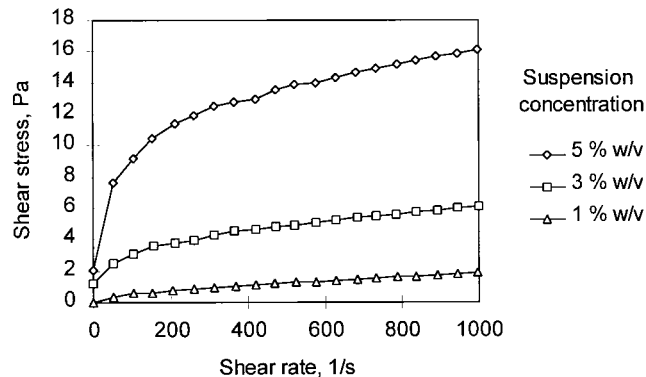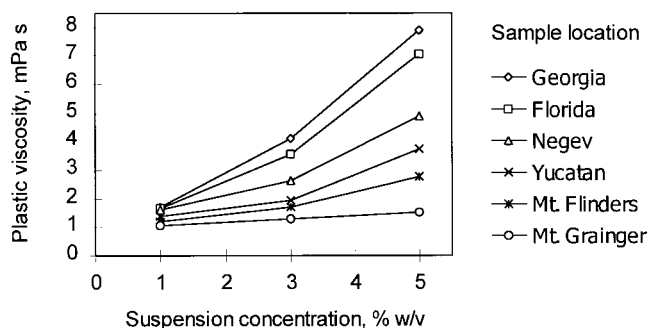
Fig. 5. Plastic viscosity of Na–palygorskite suspensions at pH 7 as a function of suspension concentration.

ming montmorillonite, while the values for the Negev sample are similar to those for Wyoming montmorillonite (Table 1). However, these rheological parameters for the Florida and Georgia samples are much higher than those for Wyoming montmorillonite. As mentioned above, the Bingham yield value and apparent viscosity of these samples are also much higher than expected from the ellipticity of the fibers, probably because of the presence of smectite impurities.

Effect of Adsorbed Ion

The effect of adsorbed Li, Na, Mg, Ca, and Ba on flow, illustrated by behavior of the Yucatan sample, is shown in Fig. 6. The flow of the suspension is much less pseudoplastic for clay saturated with monovalent ions than that for clay saturated with divalent ions. Table 3 summarizes the effect of adsorbed ion on the rheology of 5% suspension of Florida and Yucatan samples at pH 7. Table 4 shows hydrated radii and limiting hydration numbers of ions in water (Israelachvili, 1992; Marcus, 1985). The plastic viscosity, Bingham yield value, and apparent viscosity of suspensions are higher for clays saturated with divalent ions than those for clays saturated with monovalent ions (Table 3). For ions of the same valency, rheological parameters increase with a decrease in hydrated radius and limiting hydration number (Tables 3 and 4). This behavior may be explained in the following way.

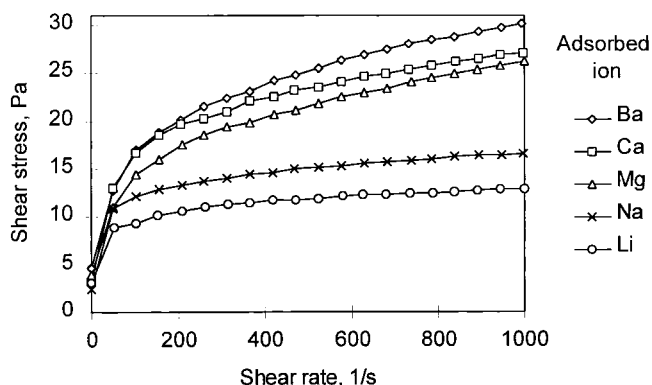As the adsorbing ions become less hydrated, the probability of finding the ion near the particle surface increases. The resultant increase of the adsorbing ion concentration in the Stern layer decreases the surface potential, and reduces the electrostatic repulsion between the particles. This effect was clearly evident with latex suspensions where the flocculation value decreased in the order (Zimehl and Lagaly, 1986): $Li^+ > Na^+ > K^+$ and $Mg^{2+} > Ca^{2+} > Ba^{2+}$. Thus, the decrease in ion hydration favors ion adsorption, which in turn reduces the repulsion between particles and therefore the flocculation value.

Repulsion between particles also depends on the valency of the adsorbed ions. Repulsive forces are weaker for divalent ion systems than those for clays containing monovalent ions with the same hydrated radius. According to the DLVO theory, a reduction in particle–particle repulsion would decrease the equilibrium distance between fibers and increase the energy of particle–particle interaction (Güven, 1992b). This, in turn, would increase the work required to break down the network of microaggregates during shearing and the resistance to flow of individual fibers. Thus, the rheological parameters of palygorskite suspensions increase as the equilibrium distances between the fibers decreases.

In all cases, the plastic viscosity of Mg–palygorskite suspensions was higher than that of Ca–palygorskite; however, the Bingham yield value and apparent viscosity of the suspensions did not follow a consistent pattern (Table 1). As discussed above, the rheological parameters of Mg–palygorskite suspensions should be lower than those of the Ca–clay, because the hydrated radius of Mg is larger than that of Ca. From this point of view, the relatively high rheological parameters of Mg–

Table 3. Effect of adsorbed ion on plastic viscosity, Bingham yield value, and apparent viscosity of Florida and Yucatan samples.

Adsorbed ion	Bingham model		Apparent viscosity at 1000 s^{-1}
	Plastic viscosity	Yield value	
	mPa s	Pa	mPa s
	Florida Sample		
Li^+	2.04	15.36	17.29
Na^+	7.05	15.89	22.57
Mg^{2+}	10.33	17.85	27.79
Ca^{2+}	9.84	19.30	28.73
Ba^{2+}	10.87	19.52	29.91
	Yucatan sample		
Li^+	2.46	10.60	12.96
Na^+	3.72	13.06	16.63
Mg^{2+}	10.31	16.24	26.16
Ca^{2+}	8.94	18.65	27.16
Ba^{2+}	11.61	19.14	30.30

Fig. 6. Flow curves of 5% (w/v) suspensions of Yucatan palygorskite adsorbed with different ions at pH 7.

Table 4. Hydrated radii and limiting hydration numbers of ions used in the study.

Ion	Hydrated radius†	Limiting hydration number‡
	nm	
Li^+	0.38	7.4
Na^+	0.36	6.5
Mg^{2+}	0.43	11.7
Ca^{2+}	0.41	10.4
Ba^{2+}	nd§	9.6

† Israelachvili: (1992).
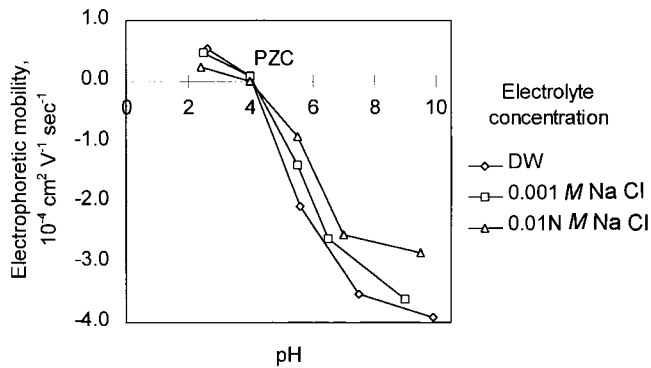‡ Marcus (1985).
§ nd is not determined.

Fig. 7. Relationship between pH and electrophoretic mobility at different electrolyte concentrations for Na–palygorskite from the Negev.

palygorskite suspensions are surprising. Palygorskite is the richest in Mg among the common clay minerals (Singer, 1989). It can be assumed that relatively high rheological parameters of Mg–palygorskite suspension, obtained in some cases, are related to the specific adsorption of Mg ions by palygorskite surfaces, which reduce the repulsion between the fibers and increase the rheological parameters.

The effect of adsorbed ions on the rheology of palygorskite suspensions deviates considerably from that of montmorillonite and kaolinite suspensions. It was reported that a 2.5% (w/v) suspension of Ca– and Mg–montmorillonites at pH 7 showed Newtonian rheology, but the flow of a Na–montmorillonite suspension was non-Newtonian, with a relatively high viscosity (Keren, 1988, 1989). The viscosity of a 5% (w/v) suspension of Ca–kaolinite at pH 7 was higher than that of Na–kaolinite, but both suspensions showed Newtonian flow (Keren, 1991).

Electrophoretic Mobility of Palygorskite

Figure 7 shows electrophoretic mobility of palygorskite from the Negev as a function of pH and electrolyte concentration. The plots of electrophoretic mobility vs. pH at different concentrations of NaCl intersect at pH 4.1. As will be shown below, this intersect represents the point of zero charge (PZC) of the palygorskite surface.

Palygorskite carries a negative charge on the basal surface of the fibers resulting from isomorphous substitution. The rate of the isomorphous substitution is low, so the magnitude of the permanent surface negative charge and the cation-exchange capacity of palygorskite are quite low. Because this charge is intrinsic to the layer structure, its sign and magnitude are independent of pH.

Structurally, palygorskite consists of alternation of blocks and tunnels that grow along the length of the fiber. Each structural block is composed of a central octahedral sheet sandwiched between two discontinuous tetrahedral sheets of silica. Due to the discontinuity of the silica sheets, silanol groups (Si-OH) are present on the surface of the fiber. These groups are located at the edges of the channels (tunnels extend to the external

surface of the silicate). Silanol groups are formed as a result of broken Si-O-Si bonds at external surfaces balancing their residual charge by accepting either protons or hydroxyl groups to form Si-OH groups (Galan, 1996).

The silanol groups at external surfaces of palygorskite can be protonated and deprotonated under acid and alkaline pH conditions, respectively. At the PZC the surface is essentially uncharged, while at pH values above and below the PZC it will be negatively and positively charged, respectively.

The change of electrophoretic mobility per pH unit is greater under alkaline than that under acid conditions (Fig. 7). It seems that protonation of silanol groups is preferred over deprotonation. The magnitude of the positive charge under acid conditions is relatively low. Analogous results for precipitated silica were presented by Lagaly (1986), who found that the silanol groups of precipitated silica were protonated at very low pH values (pH 2).

Besides being dependent on pH, the electrophoretic mobility is sensitive to variations in electrolyte concentration. By compressing the electrical double layers, electrolyte additions will reduce the absolute value of electrophoretic mobility. Electrophoretic mobility becomes less positive with addition of electrolyte under acidic conditions and less negative under alkaline conditions (Fig. 7). The plots of electrophoretic mobility of palygorskite from the Negev vs. pH at different concentrations of NaCl intersect at pH 4.1. This point represents the PZC of the palygorskite surface. A very similar PZC at pH 4.5 was measured for the Mt. Flinders palygorskite (data not shown).

Thus, the silanol groups on the external surfaces of palygorskite can affect the surface charge and can also play an important role in the rheological properties of palygorskite suspensions. Similar conclusions were presented by Aznar et al. (1992) for sepiolite suspensions. The adsorption of Methylene Blue (MB) on sepiolite gels was investigated in the study by spectroscopic and rheological methods. It was found that the progressive coverage of the sepiolite surface by MB produces a sharp decrease in the viscosity of the gels, and the suspension becomes peptized. These results indicate that MB interferes in particle–particle interactions. The decrease in viscosity is parallel to the perturbation of the Si-OH groups on the sepiolite surface as observed by IR spectroscopy, suggesting that silanol groups can play an important role in rheological behavior of sepiolite suspension.

Effect of pH on Particle Arrangement

In suspensions at low pH values the particles of palygorskite are likely to adopt a face-to-face association. In order to check this point, suspensions of the Negev palygorskite were examined by scanning electron microscopy (SEM). SEM images indicate significant differences in fiber arrangement between low and high pH values. Figure 8 shows the arrangement of the Negev palygorskite fibers in suspension. Figures 8a and 8b

show that fibers form close-packed domains in suspension at pH 3. Groups of parallel fibers are associated by face-to-face contacts. Figures 8c and 8d show that in suspension at pH 10 the fibers adopt a random orientation. A similar fiber arrangements at low and high pH values were observed for the Florida palygorskite (not shown).

Thus, when the pH of the suspension is 3.0 (a value that is below the PZC of the palygorskite surface), the net electrostatic charge of the surface is slightly positive. Under these conditions, van der Waals attraction predominates over electrostatic repulsion. "T"-like edge-to-face contacts are expected in palygorskite suspension at pH values below PZC similar to what is reported for kaolinite suspensions by Rand and Melton (1975, 1977). No "T"-like edge-to-face contacts occurred in palygorskite suspensions at low pH values. The domains of the parallel-oriented fibers were arranged in the suspension by face-to-face contacts (Fig. 8a and 8b). When the pH of the suspension is 10.0 (a value which is well above the PZC of the palygorskite surface), the net electrostatic charge of the surface is negative. Under these conditions the single palygorskite fibers repel each other and no domains are formed in the suspension (Fig. 8c and 8d).

The concept of electrostatic attractive forces between the positively charged edges and negatively charged faces of clay particles at pH values below the PZC has been applied successfully to kaolinite suspensions to explain the influence of pH and electrolyte on the rheological parameters (Rand and Melton, 1975, 1977). However, this model does not account for the behavior of palygorskite suspensions because the surface structure and particle morphology of palygorskite are different from those of kaolinite. The effect of pH on particle arrangement in palygorskite suspensions at low pH values also deviates from that in montmorillonite suspensions where edge-to-edge association is the primary mode of particle interactions and is responsible for the pseudoplastic behavior of the suspension (Keren, 1988, 1989).

Effect of pH

The effect of pH on flow, illustrated by behavior of the Negev palygorskite, is shown in Fig. 9. Suspensions of pH $\geq$ 9 exhibited near-Newtonian flow. At pH $\geq$ 9, the fibers of palygorskite tend to repel each other because the magnitude of the negative surface charge is high. As a result, individual particles can move independently under flow and the system exhibits a near-Newtonian flow with a very small yield stress and a low viscosity.

At pH 7 and below, palygorskite fibers form microaggregates because the magnitude of the negative surface charge is relatively low and van der Waals attraction predominates over electrostatic repulsion, and the suspensions exhibit non-Newtonian flow with a high viscosity.

The effect of pH on the rheology of palygorskite is similar to that of montmorillonite. Keren (1988) reported that both the apparent viscosity and the yield
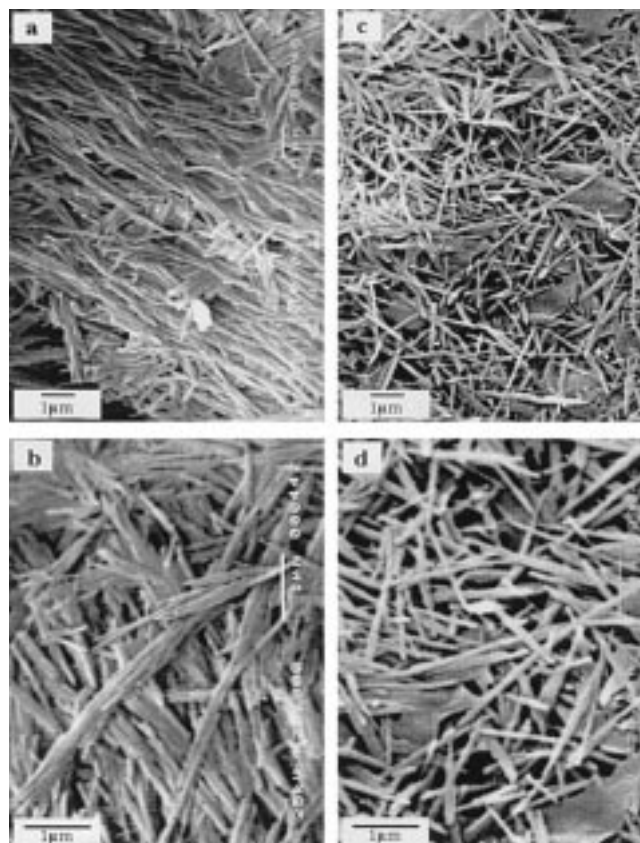

Fig. 8. Scanning electron micrographs of Na–palygorskite from the Negev showing differences in arrangement of fibers in suspension between low and high pH values: (a, b) pH 3 at different magnifications and (c, d) pH 10 at different magnifications.

stress of 2.5% (w/v) suspensions of Na–montmorillonite decreased with increasing pH from 7 to 10. Non-Newtonian flow at pH 7 and Newtonian flow at pH 10 were observed. Permien and Lagaly (1995) reported that the yield value of a 2.2% (w/v) suspension of Na–montmorillonite was high at pH 3, but decreased dramatically with increasing pH, reaching a minimum at pH $\approx$4.5. At pH > 4.5, yield values increased again, showing a maximum at pH $\approx$7. The yield values decreased again at pH > 7. However, the effect of pH on the rheology of Na–montmorillonite depends on solid content. Heath
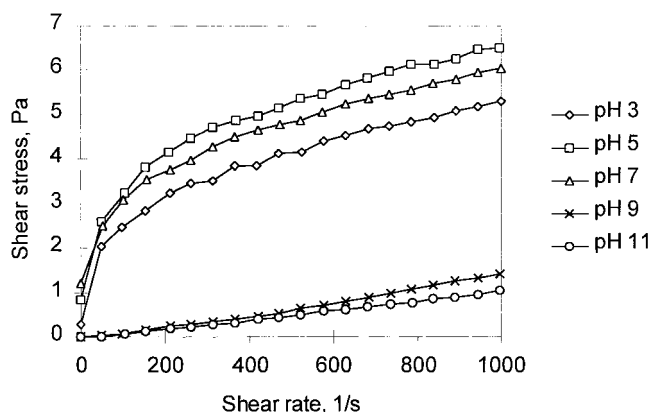

Fig. 9. Flow curves of 3% (w/v) suspensions of Na–palygorskite from the Negev at different pH values.
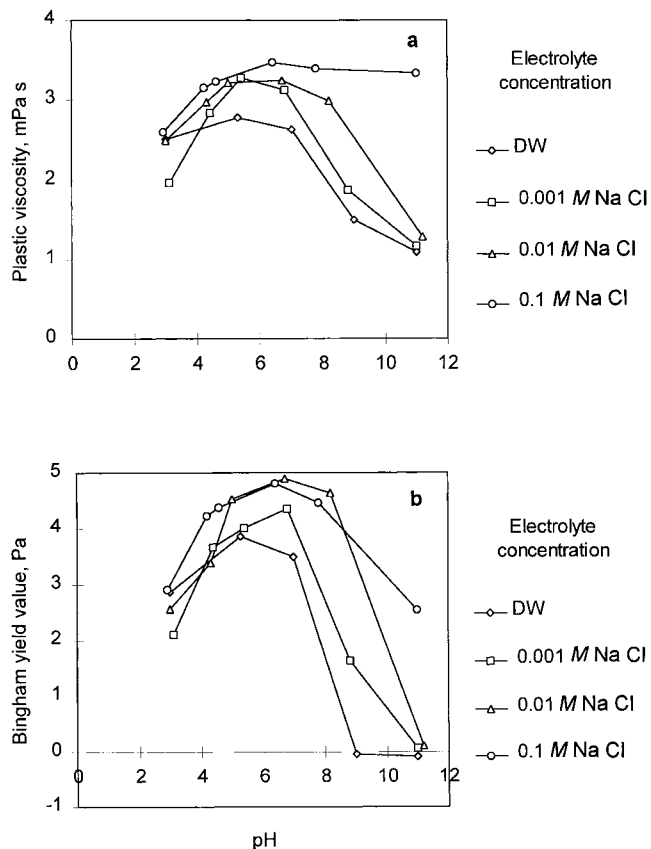
Fig. 10. The effect of electrolyte addition on (a) plastic viscosity and (b) Bingham yield value of 3% (w/v) suspensions at different pH values for Na–palygorskite from the Negev.

and Tadros (1983), Brandenburg and Lagaly (1988) and Lagaly (1989) reported that yield values of 4% (w/v) suspensions of Na–montmorillonite showed a sharp minimum at pH ≈7 and increased on either side of the neutral pH. Thus, the minimum in yield values of 2.2 to 2.5% suspensions at pH ≈4.5 is shifted to pH ≈7 in the case of 4% (w/v) suspensions. With higher solid concentrations, a more drastic increase in pH is required in order to disrupt the edge-to-face associations that are responsible for the high yield values at low pH (Lagaly et al., 1997).

The curves in Fig. 9 indicate that both the Bingham yield and plastic viscosity are lower at pH 3 than at pH 5 to 7. As discussed above, the fibers form close-packed domains by face-to-face contacts at pH 3. It is suggested that these domains can move independently under applied stress. Formation of close-packed domains decreases the number of particles in suspension, which in turn decreases the plastic viscosity of the suspension. At the same time, the distance between particles increases, which fragments the network structure and decreases the Bingham yield value.

Brandenburg and Lagaly (1988) also reported that the yield stress of a 4% (w/v) suspension of Na–montmorillonite decreased as the pH fell below 4.5. These authors attributed the decrease in yield stress to the aggregation of particles into clusters of finite sizes that moved independently under applied stress.

At pH 5 and 7 the high magnitude of negative surface charge prevents the formation of close-packed domains in palygorskite suspensions. Nevertheless, particle–particle interaction apparently occurs because the flow is pseudoplastic. It is suggested that at pH 5 and 7 loose-packed domains are formed, giving rise to a "scaffolding structure" (van Olphen, 1977). This structure breaks down under applied stress and suspensions show a relatively high yield stress and viscosity.

Effect of Electrolyte Addition

Figure 10 shows the effect of electrolyte additions on the plastic viscosity and Bingham yield value of suspensions of the Negev palygorskite at different pH values. At pH <7 these parameters are only slightly affected by electrolyte addition, remaining relatively constant even at high electrolyte concentrations. However, the same parameters are significantly influenced by electrolyte addition at pH >9. Similar results were observed for the Florida palygorskite (not shown).

The effect of electrolyte addition on the rheology of palygorskite suspensions deviates significantly from that of montmorillonite suspensions. Chen et al. (1990) and Permien and Lagaly (1994) reported that yield values of Na–montmorillonite decreased with addition of low amounts of NaCl, showing the minimum at a concentration of 0.005 mol L^{-1}. Further addition of NaCl (up to 0.1 mol L^{-1}) increases the yield values sharply. Heath and Tadros (1983) reported that the effect of NaCl addition on plastic viscosity was significant at alkaline pH values, but not well defined at neutral and acid pH values.

Palygorskite has a wide range of industrial applications, one of which is its usage as drilling muds. Palygorskite muds have the advantage over other clays (such as smectite) in being less sensitive to salts; the desired rheological properties remain virtually constant even at high electrolyte concentrations at pH <9 (Galan, 1996). The findings of our present study are in agreement with this industrial experience.

As noted above, at pH ≤ 7, palygorskite fibers form microaggregates because the magnitude of the negative surface charge is low and van der Waals attraction predominates over electrostatic repulsion. The addition of electrolytes increases the plastic viscosity and the Bingham yield value by compressing the electrical double layers, thus lowering the energy barrier to van der Waals attraction. The influence of electrolyte addition is slight, because the initial magnitude of the negative surface charge is low and electrostatic repulsion is weak. At pH ≥ 9, the fibers of palygorskite tend to repel each other since the magnitude of the negative surface charge is high. As a result, individual fibers of palygorskite can move independently under flow. The addition of electrolyte to palygorskite suspensions at pH ≥ 9 significantly increases the plastic viscosity and Bingham yield value due to coagulation of the system. Similar results were reported by Haden and Schwint (1967) and Ovcharenko (1963).

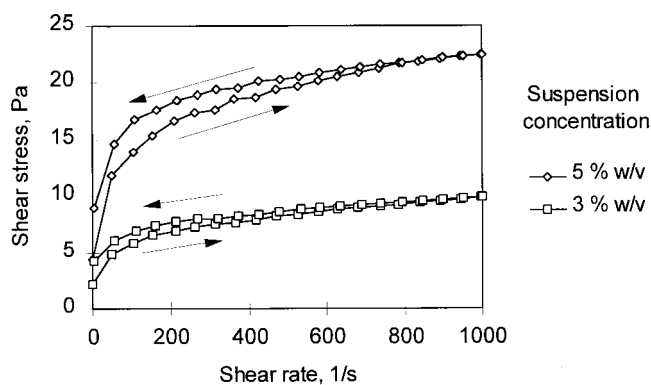The gelling mechanism of palygorskite is different

Fig. 11. Flow curves of 3 and 5% suspensions of Na–palygorskite from Florida at pH 7 showing antithixotropic behavior of the suspensions.

Fig. 12. The effect of pH on hysteresis loop area enclosed by flow curves of 3% suspensions of Na–palygorskite from Florida at different electrolyte concentrations. The area of hysteresis loop is accepted to be positive if the behavior of the system is thixotropic and negative if the behavior is antithixotropic.

from that of layer silicates like montmorillonite. Montmorillonite saturated with Na^+ shows osmotic swelling and gelling when immersed in water or dilute aqueous solutions of an electrolyte (Borchardt, 1989). In contrast, palygorskite does not show intracrystalline swelling because of the chain-like structure and the low isomorphous substitution. Palygorskite tends to form aggregates and does not show spontaneous dispersion in water. Aggregate separation into individual fibers cannot be achieved by hydration of interlayer cations as in montmorillonite, but separation is possible by mechanical means such as mixing at high speed (Kheng, 1989) or ultrasonication (the present study).

Since gelling in palygorskite does not requires osmotic swelling, palygorskite gels can be prepared in water and other solvents without concern for the exchangeable cations or electrolytes present.

Thixotropy and Rheopexy of Palygorskite Suspensions

From a rheological point of view, thixotropy is defined as the isothermal and reversible gel-liquid transformation upon mechanical agitation (Güven, 1992a). A thixotropic system begins to flow under stirring and thickens again when standing. Such a suspension will change during flow curve measurements by a viscometer, and a hysteresis loop will be obtained when readings are taken subsequently at increasing and decreasing rates of shear. In other words, thixotropy is a time-dependent phenomenon. The network structure of the semirigid gel appears to be broken by shear forces and the interparticle bonds tends to reestablish themselves with time (Güven, 1992a; Lagaly, 1989).

Antithixotropy or rheopexy is a phenomenon that is just the opposite of thixotropy. The increase in the rate of stiffening due to shearing of the suspension is a consequence of the enhanced collision frequency in a stirred system. Under shearing, particles may be linked together into a three-dimensional network and form a gel.

Thixotropy is an important characteristic for industrial applications. For example, drilling fluids and paints must be thixotropic. Palygorskite suspensions are thixotropic and, for that reason, have a wide range of industrial applications (Galan, 1996). Surprisingly, elec-
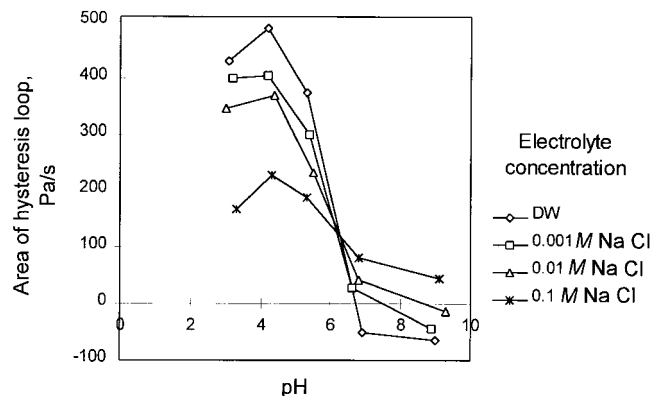
trolyte-free palygorskite suspensions at pH 7 are antithixotropic. This behavior was observed for all palygorskite samples used in the study and was not dependent on adsorbed ion. Figure 11 shows flow curves of 3 and 5% suspensions of Na–palygorskite from Florida at pH 7. Antithixotropy is indicated by the hysteresis loop of the flow curves.

The area of the hysteresis loop of the flow curves, which is a measure of the degree of hysteresis, is accepted to be positive if the behavior of the system is thixotropic, and negative if the behavior is antithixotropic. The degree of hysteresis decreases with increasing pH and increases with electrolyte concentration (Fig. 12). The process of thixotropic stiffening is essentially the same as slow coagulation in a dilute suspension. With increasing electrolyte concentration and decreasing pH, the negative charge of palygorskite surfaces is reduced (Fig. 7) and the rate of particle linking and stiffening of the suspension increases. Plots of hysteresis loop area vs. pH at different concentrations of NaCl intersect at pH 6.4 (Fig. 12). This indicates that at this pH the degree of hysteresis is independent of charge density and, therefore, of electrolyte concentration.

These results suggest that palygorskite suspensions are thixotropic if they are in a coagulated state (at low pH values and high electrolyte concentrations) and antithixotropic if they are in a dispersed state. Thixotropic behavior of palygorskite suspensions in industry can be achieved by addition of different components that cause their coagulation.

Hohenheim, Germany, and the Hebrew University of Jerusalem, Israel, Agreement of Cooperation.

REFERENCES

Aznar, A.J., B. Casal, E. Ruiz-Hitzky, I. Lopez-Arbeloa, F. Lopez-Arbeloa, J. Santaren, and A. Alvarez. 1992. Adsorption of methylene blue on sepiolite gels: Spectroscopic and rheological studies. Clay Miner. 27:101–108.

Borchardt, G. 1989. Smectites. p. 675–727. In J. Dixon and S. Weed (ed.) Minerals in the soil environments. 2nd ed. SSSA Book Ser. 1. SSSA, Madison, WI.

Brandenburg, U., and G. Lagaly. 1988. Principles of flow of kaolin and bentonite dispersions. Appl. Clay Sci. 4:105–123.

Brindley, G.W. 1980. Quantitative x-ray mineral analysis of clays. p. 411–438. In G.W. Brindley and G. Brown (ed.) Crystal structures of clay minerals and their x-ray identification. Mineralogical Soc., London.

Chen, J.S., J.H. Cushman, and P.F. Low. 1990. Rheological behavior of Na–montmorillonite suspensions at low electrolyte concentration. Clays Clay Miner. 38:57–62.

Dixon, J., and S. Weed (ed.). 1989. Minerals in the soil environments. 2nd ed. SSSA Book Ser. 1. SSSA, Madison, WI.

Einstein, A. 1906. Eine neue bestimmung der molekuldimension. Ann. Physik. 19:289–306.

Galan, E., J.M. Mesa, and C. Sanchez. 1994. Properties and applications of palygorskite clays from Ciudad Real, Central Spain. Appl. Clay Sci. 9:293–302.

Galan, E. 1996. Properties and applications of palygorskite-sepiolite clays. Clay Miner. 31:443–453.

Güven, N. 1992a. Rheological aspects of aqueous smectite suspensions. p. 81–125. In N. Güven and R.M. Pollastro (ed.) Clay–water interface and its implications. CMS Workshop Lectures. Vol. 4. Clay Minerals Soc., Boulder, CO.

Güven, N. 1992b. Molecular aspects of clay/water interactions. p. 1–79. In N. Güven and R.M. Pollastro (ed.) Clay–water interface and its implications. CMS Workshop Lectures. Vol. 4. Clay Minerals Soc., Boulder, CO.

Haden, W L., and I.A. Schwint. 1967. Attapulgite: Its properties and applications. Ind. Engin. Chem. 59:58–69.

Heath, D., and T.F. Tadros. 1983. Influence of pH, electrolyte, and poly(vinyl alcohol) addition on the rheological characteristics of aqueous dispersions of sodium montmorillonite. J. Colloid Interf. Sci. 93: 307–319.

Hofmann, U., and A. Hausdorf. 1945. Über das sedimentvolumen und die quellung von bentonit. Kolloid Z. 110:1–17.

Israelachvili, J.N. 1992. Intermolecular and surface forces. 2nd ed. Academic Press, London.

Kahn, A. 1959. Studies on the size and shape of clay particles in aqueous suspension. p. 220–236. In A. Swineford (ed.) Proc. 6th Natl. Conf. Clays Clay Miner. Berkeley, CA. 19–23 Aug. 1957. Vol. 8. Pergamon Press, London.

Keren, R. 1988. Rheology of aqueous suspension of sodium/calcium montmorillonite. Soil Sci. Soc. Am. J. 52:924–928.

Keren, R. 1989. Effect of clay charge density and adsorbed ions on the rheology of montmorillonite suspension. Soil Sci. Soc. Am. J. 53:25–29.

Keren, R. 1991. Adsorbed sodium fraction's effect on rheology of montmorillonite–kaolinite suspensions. Soil Sci. Soc. Am. J. 55: 376–379.

Kheng, H.Y. 1989. Rheological and physico-chemical properties of palygorskite clay and anionic polyacrylamide polymer slurries used in drilled shaft constructions. Ph.D. thesis. Univ. Florida, Gainesville.

Klute, A. (ed.) 1986. Methods of soil analysis. Part 1. 2nd ed. ASA and SSSA, Madison, WI.

Lagaly, G. 1986. Colloids. p. 341–367. In Ullmann's encyclopedia of industrial chemistry. Vol. A7, VCH Verlagsgesellschaft, Weinheim, Germany.

Lagaly, G. 1989. Principles of flow of kaolinite and bentonite dispersions. Appl. Clay Sci. 4:105–123.

Lagaly, G., O. Schulz, and R. Zimehl. 1997. Dispersionen und emulsionen: Eine einführung in die kolloidik feinverteilter stoffe einschließlich der tonminerale. Steinkopff, Darmstadt, Germany.

Marcus, Y. 1985. Ion solvation. John Wiley and Sons, Chichester, UK.

Neaman, A., and A. Singer. 2000. Kinetics of palygorskite hydrolysis in dilute salt solutions. Clay Miner. (In press).

Ovcharenko, F.D. (ed.) 1963. The colloid chemistry of palygorskite. Acad. Sci. Ukr. SSR, Kiev. (In Russian).

Permien, T., and G. Lagaly. 1994. The rheological and colloidal properties of bentonite dispersions in the presence of organic compounds: I. Flow behavior of sodium-bentonite in water-alcohol. Clay Miner. 29:751–760.

Permien, T., and G. Lagaly. 1995. The rheological and colloidal properties of bentonite dispersions in the presence of organic compounds: V. Bentonite and sodium montmorillonite and surfactants. Clays Clay Miner. 43:229–236.

Pupisky, H., and I. Shainberg. 1979. Salt effects on the hydraulic conductivity of a sandy soil. Soil Sci. Soc. Am. J. 43:429–433.

Rand, B., and I.E. Melton. 1975. Isoelectric point of the edge surface of kaolinite. Nature (London) 257:214–216.

Rand, B., and I.E. Melton. 1977. Particle interactions in aqueous kaolinite suspensions, I. Effect of pH and electrolyte upon the mode of particle interaction in homoionic sodium kaolinite suspensions. J. Colloid Interf. Sci. 60:308–320.

Shainberg, I., and H. Otoh. 1968. Size and shape of montmorillonite particles saturated with Na/Ca ions. Isr. J. Chem. 6:251–259.

Singer, A. 1989. Palygorskite and sepiolite group minerals. p. 829–872. In J. Dixon and S. Weed (ed.) Minerals in the soil environments. 2nd ed. SSSA Book Ser. 1. SSSA, Madison, WI.

van Olphen, H. 1977. An introduction to clay colloid chemistry. 2nd ed. John Wiley and Sons, New York.

Zimehl, R., and G. Lagaly. 1986. Coagulation of latex dispersions by inorganic salts structural effects. Progr. Colloid Polymer Sci. 72: 28–36.