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ORIGINAL CONTRIBUTION

M.P. Lott
D.J.A. Williams
P.R. Williams

The elastic properties of sodium montmorillonite suspensions

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M.P. Lott · D.J.A. Williams · P.R. Williams
Horsell Graphic Industries Ltd.
Morley Leeds

M.P. Lott · Prof. Dr. D.J.A. Williams (✉)
P.R. Williams
Department of Chemical Engineering
University of Wales Swansea
Singleton Park
Swansea SA2 8PP, Wales, United Kingdom

Abstract Shear wave rigidity moduli G have been determined using a shear wave propagation technique for sodium montmorillonite suspensions. Measurements were made as a function of time at various values of pH, NaCl concentration (C) and solids concentration and the data used to estimate G_e the value of the modulus at $t = \infty$. The dependency of G_e on pH, C and solids concentration is interpreted in terms of the mode of interaction between particles and the associated volume filling structure. The results suggest that whether a coagulated or dispersive structure develops in these suspensions depends not only on pH and C but also on the degree of delamination of the clay.

Key words Sodium montmorillonite suspensions – shear wave propagation – elasticity – wave rigidity modulus

Introduction

Despite its fundamental and practical importance few detailed investigations of the elastic behaviour of sodium montmorillonite suspensions have been published. Callaghan and Ottewill [1] determined an elastic modulus using a compression cell and considered the elastic response of carefully prepared sodium montmorillonite suspensions in dilute NaCl to be due to long-range electrostatic interactions. Rand et al. [2] using a shear wave propagation technique found time-dependent shear moduli $G(t)$ for treated suspensions to be sensitive to NaCl concentration at pH 7.3. More recently Khandal and Tadros [3] and Sohm and Tadros [4] have made measurements of $G(t)$ in conjunction with other viscoelastic parameters obtained from dynamic oscillation measurements to assess the kinetics of gelation of montmorillonite suspensions. Marked differences were found in the variation with pH of an equilibrium shear modulus estimated graphically from $G(t)$ data for two different commercial clays. However the clay surfaces were not treated prior to rheological testing and the type and concentration of electrolyte was unknown.

It is evident that a systematic investigation of the influence of pH, concentration of NaCl and solids concentration on the elastic behaviour of homoionic sodium montmorillonite suspensions is desirable. This is addressed in the present paper using a shear wave propagation technique. A particular objective of this work is to gain further insight into the nature of particle interactions and associated structures in these suspensions, a subject which continues to be of theoretical interest [5, 6].

Experimental

All reagents were of Analar grade. Water treated by reverse osmosis (single stage), a combination of mixed bed ion exchange and adsorption over activated carbon and finally micro-filtration (Elgastat Spectrum R) to give a conductivity of approximately 0.4×10^{-6} Siemens, was used throughout.

The clay (BDH Chemicals Ltd., U.K.) was a montmorillonite from Wyoming (S. Dakota, Black Hills)

Preparation of clay

The clay was converted into the homoionic form using the following procedure. Aqueous 2% (*w*/*v*) dispersions (pH ~ 8.0) of raw clay were treated with H_2O_2 to remove organic matter and subjected to sedimentation to remove the coarse fraction of particles. The fine fraction was washed with 1 M NaCl, agitated frequently and allowed to stand for a period ≥ 24 h. The clay was removed by centrifugation, redispersed to form a 2% (*w*/*v*) dispersion and washed again with NaCl. The resulting clay dispersion was dialysed (Visking tubing) against water to remove excess salt. The procedure was terminated once the conductivity of the dialysate remained unchanged over several days ($\leq 10 \times 10^{-6}$ Siemens). The level of aluminium in the supernatant liquid of the homoionic clay dispersions was determined using the method of Dougan and Wilson [7]. At low pH (≤ 4.5) the concentration was ≤ 9 μg/l, which suggests that a washing step at pH 3 used by others (see e.g. Horikawa et al. [8]) was unnecessary for this clay.

Clay dispersions were finally passed through a sintered glass filter (Gallenkamp Sinter glass 3; 15–40 μm) and then into a 10 l flask to produce a stock dispersion. Aliquots of this material were dried (60 °C) to constant mass thereby providing solid Na-montmorillonite from which dispersions of varying weight fractions ϕ_w were prepared by adding the required mass of clay to the appropriate electrolyte with ultrasonication for 5 h to ensure adequate dispersion of the solids in the electrolyte. pH was adjusted by dropwise addition of HCl or NaOH. Dispersions were allowed to equilibrate for 48 h before rheological testing. Samples at pH > 7 were purged with N_2 (British Oxygen, U.K.; CO_2 free) prior to equilibration.

Size and density

Electron microscopic examination (Jeol Ltd., Model 120C TEMSCAN) of the clay revealed particles with a predominantly platy habit with average diameter and thickness of 480 nm and 40 nm respectively [9]. The latter figure suggests face-face aggregation since the unit layer thickness of montmorillonite is ~0.96 nm [10].

The density of clay dried to constant mass (60 °C) was determined using specific gravity bottles (25 °C) and found to be 2340 kg/m^3 (+ / − 10 kg/m^3).

Shear wave propagation

Values of the shear wave rigidity modulus *G* were determined using a modification [11] of a pulse shearometer (Rank Bros., Bottisham, Cambridge, U.K.). In a version of the instrument the test sample [~ 10 ml] is held in a cylindrical perspex chamber (27 mm internal diameter) housing two parallel stainless steel plates (25 mm diameter). These plates, supported by steel stalks, are mounted above and in intimate contact with two piezo-electric crystals in perspex mounts. The plate separation may be varied by either a quick release mechanism, enabling large movement of the upper plate, or by means of a vernier screw gauge attached to the upper plate housing enabling finer adjustments (+ / − 10 μm) to be made.

A signal generator supplies a transient electrical pulse to the lower crystal which causes a small displacement of the lower plate in its own plane (typically $< 10^{-4}$ rads), initiating shear wave propagation between the plates. The frequency (f) of the wave is ~300 Hz; its velocity V is determined by measuring the time t_F taken by the wave to travel the distance between plates.

The dynamic modulus G' is related to V by

$$G' = \frac{V^2 \rho (1 - r^2)}{(1 + r^2)^2} , \tag{1}$$

where ρ is the density of the sample and r is a damping factor given by

$$r = \lambda_s / 2\pi Z_0 , \tag{2}$$

where $\lambda_s (= V/f)$ is the wavelength of the shear wave and Z_0 is the damping length.

For small r (i.e., $\lambda_s/Z_0 \ll 1$), G^1 is approximated by the wave rigidity modulus

$$G = \rho V^2 . \tag{3}$$

The variation in shear wave amplitude with distance is of the form (12)

$$v = v_0 \exp(-Z/Z_0) , \tag{4}$$

where v is the wave amplitude (expressed in terms of voltage output) at the distance Z.

Z_0 is readily determined from a plot of $\ln v$ versus Z and attenuation was checked for several low solids concentrations. In each case λ_s/Z_0 was < 0.1 thus Eq. (3) was used in the present work.

The timing of measurements commenced immediately after a sample was shaken prior to its transfer to the shearometer. The first measurement of t_F was taken after 30 s; subsequent measurements were made at intervals of 30 s or longer depending on the rate of change of t_F. The time limit for each test was set at 2 h after which time it could not be assumed that any further change in G was due primarily to change in structure, but possibly due to the sample drying out.

Results

The variation of shear modulus G with time at various concentrations of NaCl at pH 7.2 is exemplified for $\phi_w = 0.07$ in Fig. 1 and as a function of pH in the presence of 5×10^{-2} M and 10^{-4} M NaCl for $\phi_w = 0.06$ in Figs. 2 and 3.

It is evident that at pH 7.2 and $C \leq 5 \times 10^{-3}$ M NaCl and at pH ≥ 5 in 10^{-4} M NaCl that G approaches an equilibrium value G_e relatively quickly in these suspensions and is readily estimated from experimental data.

For $C > 5 \times 10^{-3}$ M and at pH 7.2 the suspensions become progressively more time dependent (Fig. 1). Similar behaviour is observed with reduction in pH for $C = 5 \times 10^{-2}$ M NaCl (Fig. 2) and as the pH is reduced below 6 in 10^{-4} M NaCl (Fig. 3). These data for $t > 0$ were fitted to the following rate equation

$$G = G_1(1 - e^{-kt}) + G_0 \tag{5}$$

using a non-linear regression procedure thereby enabling $G_e(= G_1 + G_0)$ the modulus at $t = \infty$ to be calculated. G_0 is a parameter evaluated at $t = 0$ and k is a rate constant.

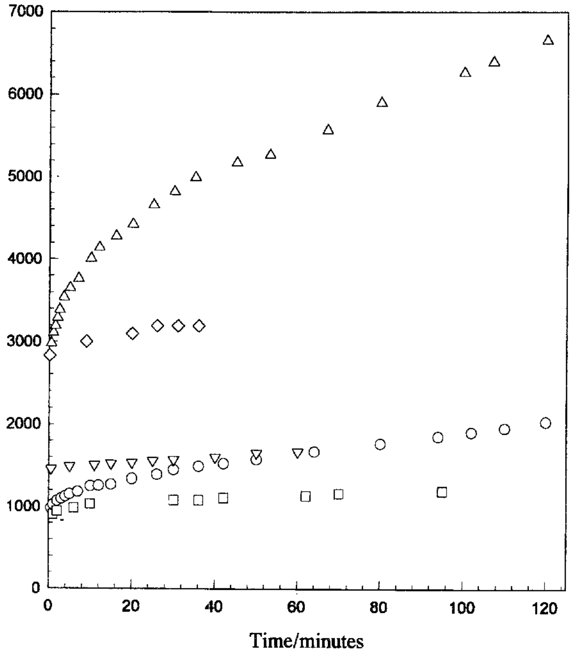

Fig. 1 Variation of G with time at $\phi_w = 0.07$; pH 7.2. ◇ 10^{-4} M NaCl; ▽ 10^{-3} M NaCl; □ 10^{-2} M NaCl; ○ 3×10^{-2} M NaCl; △ 5×10^{-2} M NaCl

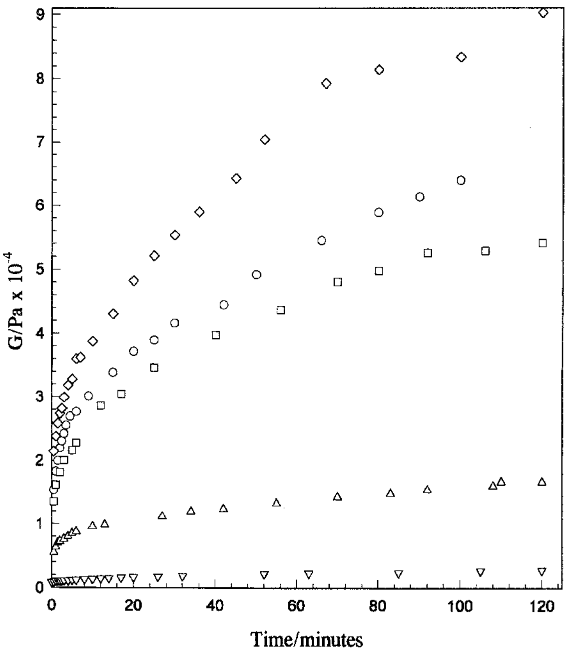

Fig. 2 Variation of G with time at various pH; 5×10^{-2} M NaCl and $\phi_w = 0.06$. ◇ pH 3.79; ○ pH 3.39; □ pH 4.4; △ pH 5.64; ▽ pH 7.2

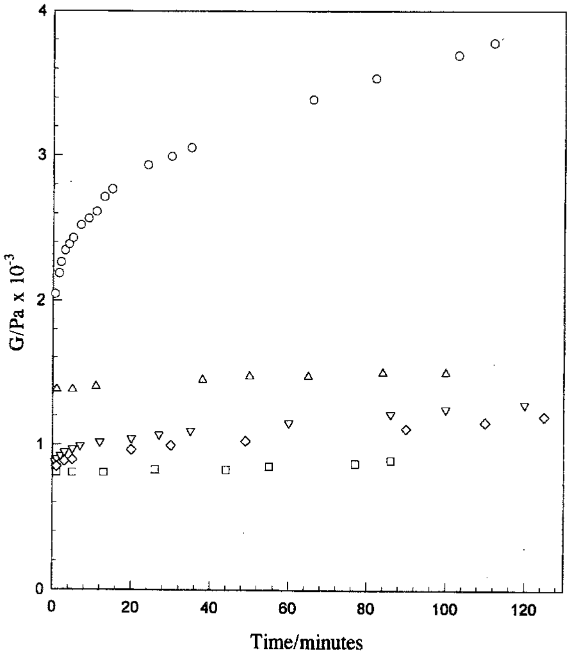

Fig. 3 Variation of G with time at various pH; 10^{-4} M NaCl and $\phi_w = 0.06$. ○ pH 3.91; ▽ pH 4.45; □ pH 5.9; △ pH 8.0; ◇ pH 4.71

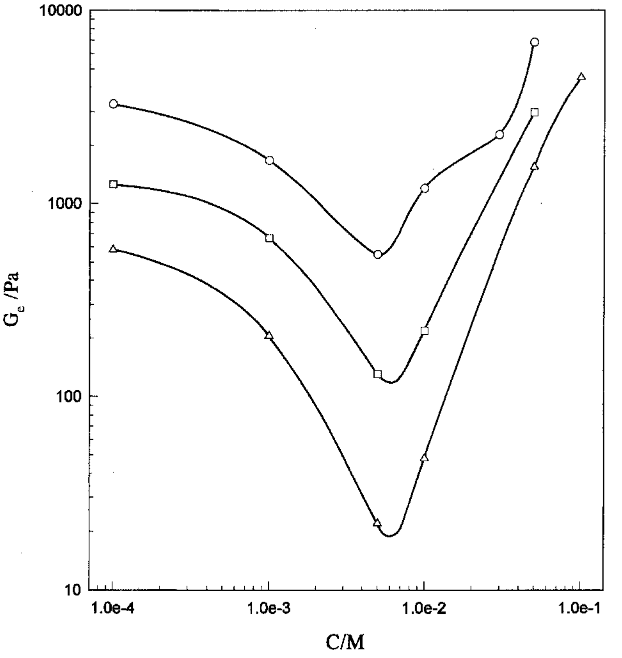

Fig. 4 Influence of NaCl concentration on G_e at pH 7.2. △ $\phi_w = 0.05$; □ $\phi_w = 0.06$; ○ $\phi_w = 0.07$

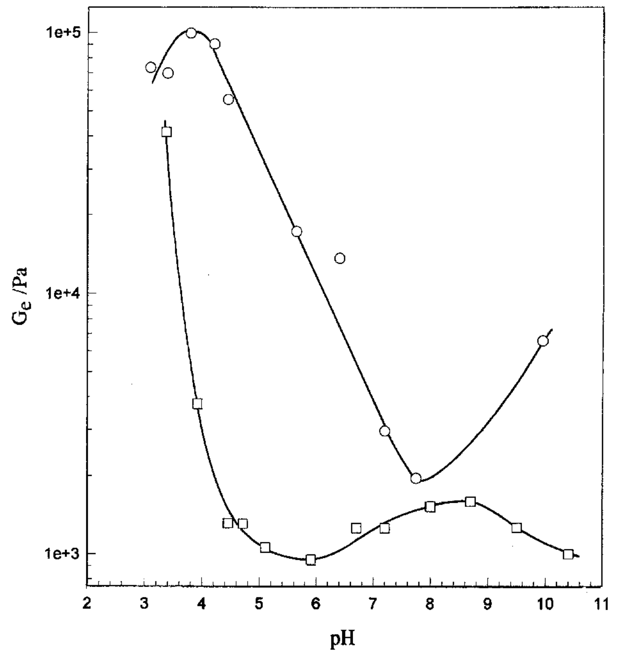

Fig. 5 Influence of pH on G_e at $\phi_w = 0.06$. ○ 5×10^{-2} M NaCl; □ 10^{-4} M NaCl

In general the standard error of G_1, G_0 and k was $< 10\%$ of the value for these parameters calculated with Eq. (5). The effect of electrolyte concentration on G_e at pH 7.2 is shown in Fig. 4 for $\phi_w = 0.05$, 0.06 and 0.07. A feature of these data is the presence of a relatively well defined minimum in G_e at 5×10^{-3} M NaCl.

The dependence of G_e on pH in 10^{-4} M NaCl and 5×10^{-2} M NaCl is shown in Fig. 5. In dilute electrolyte there is an increase in the modulus as pH is reduced from 10.4 to about 8.5. Further reduction in pH is accompanied by a decline in G_e until about pH 4.2 where the modulus increases significantly from about 1.3×10^3 Pa to 40×10^3 Pa at pH 3.4. In the more concentrated electrolyte G_e increases as pH is reduced below 7.5 with a maximum near pH 4, while above pH 8 there is evidence that G_e increases with pH.

The influence of ϕ_w on G_e at pH 7.2 is revealed in Figs. 4 and 6. Linear extrapolation of the data of Fig. 6 indicates that at pH 7.2 the structure in these suspensions becomes volume filling at weight fractions of about 0.035 and 0.01 in NaCl concentrations of 10^{-4} M and 5×10^{-2} M respectively.

Representation of these data in terms of a power law relationship

$$G \sim \phi^m , \tag{6}$$

where ϕ = the volume fraction of solids was satisfactory for 10^{-4} M NaCl with $m = 5.6$ for $0.0175 \leq \phi \leq 0.0334$ (least squares fit; correlation coefficient $r = 0.99$) but less satisfactory at 5×10^{-2} M NaCl with $m = 2.2$ for $0.0086 \leq \phi \leq 0.0311$ with ($r = 0.965$).

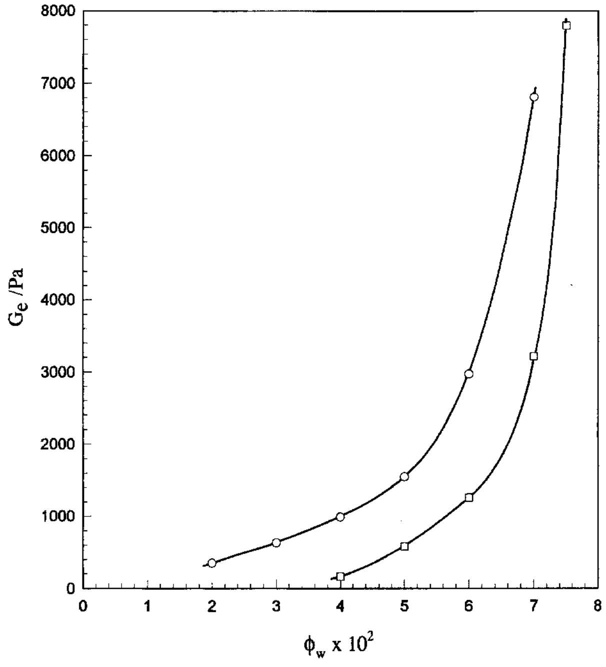

Fig. 6 Influence of solids concentration (ϕ_w) on G_e at pH 7.2. ○ 5×10^{-2} M NaCl; □ 10^{-4} M NaCl

Discussion

Montmorillonite is an expandable three-layer clay which delaminates in dilute aqueous dispersion to form anisometric platelets of thickness $\delta \geq 1$ nm [13]. In aqueous suspensions these platelets are dually charged. The negative charge on the faces (f) of the platelets is the result of isomorphous substitution in octahedral alumina and tetrahedral silica layers by the replacement of Si^{4+} by Al^{3+} or Al^{3+} by Mg^{2+} and is assumed to be independent of pH. The edge (e) is thought to behave as an oxide and possess a negative charge at values of pH above its isoelectric point (iep) while below the iep the edge will have a positive charge. Although precise estimates of the iep are precluded due to non-ideality of the edge surface, clay origin and its treatment, it is clear that the electrical potentials associated with the faces and the edges may differ in magnitude and sign depending on pH, concentration of electrolyte, ionic species and δ (5, 6, 14, 15,) and as a consequence the platelets may interact in a variety of geometric modes e.g. f-f, f-e, or e-e depending on physicochemical environment.

Two kinds of volume filling structure can be anticipated in montmorillonite suspensions depending on electrolyte concentration, pH and δ. For pH > iep and in sufficiently dilute NaCl, extended electrical double layers may interact to give an electrostatically stabilised or dispersive structure. In NaCl concentrations greater than a critical coagulation concentration (ccc) the double layers are compressed allowing van der Waals' forces to overwhelm double-layer repulsion and a coagulated or cohesive structure is formed.

The dependency of G_e on NaCl concentration (Fig. 4) reflects the existence of dispersive and cohesive structures in the present clay suspensions at pH 7.2, the transition between them occurring at a NaCl concentration of 5×10^{-3} M. This value of C corresponding to the minimum in G_e at all three weight fractions is similar to a ccc for Na^+ of 3.5×10^{-3} M for sodium montmorillonite dispersions in the mid pH range found by Swartzen-Allen and Matijevic [16].

If it be assumed that the iep of the edge is ca. pH 6–7 [15] then the edge surfaces at pH 7.2 possess a negative charge and it is most probable that at the ccc platelets coagulate in e-e mode [2]. The increase in G_e with C above 5×10^{-3} M NaCl is thus due to the increasing van der Waals' attraction between edge surfaces. While the e-e mode of interaction is likely to be the dominant one, additional interaction between similarly charged faces and edges becomes possible with increasing C.

The cohesive structure which evolves from such interactions comprises aggregates of platelets which, aided by some f-e coagulation, link together to form a network which becomes volume filling at a low critical volume fraction (ϕ_c) of about 0.0043 in 5×10^{-2} M NaCl. Above ϕ_c the rigidity modulus increases almost linearly with solids concentration becoming quite non-linear for $\phi \geq 0.0175$. These different dependencies of G_e on ϕ may be attributed to two levels of cohesive structure in these suspensions. For small increases in ϕ above ϕ_c the number of network links are proportional to solids content but for $\sim\phi \geq 0.0175$ interpenetration of aggregates occurs and there is a marked increase in G_e. For these conditions G_e is well represented by Eq. (6) with $m = 3.32$ (correlation coefficient $r = 0.98$) which value is approaching a theoretical value of 3.4 (cited by Buscall et al. [17]) associated with a structure of interpenetrating fractal aggregates formed under diffusion limiting conditions.

At pH 7.2 and for $C < 5 \times 10^{-3}$ M NaCl these suspensions are stable against coagulation. An estimate of the distance of separation (h) between particles under these conditions can be made if it be assumed they form a parallel array [18, 19] so that

$$h = \frac{2nW}{MS}, \qquad (7)$$

where W is the volume of liquid in a suspension containing M(kg) of montmorillonite, n is the number of platelets forming a particle of thickness δ and S is the specific surface area of a single platelet.

For a fully delaminated clay $n = 1$ whence taking $S = 80 \times 10^4$ m^2/kg [18] gives $h = 69$ nm for $\phi_w = 0.035$ the critical sample spanning concentration at 10^{-4} M NaCl and pH 7.2. At this separation a strong double layer interaction would be expected. However at this solids concentration $G_e \rightarrow 0$ (Fig. 6) implying negligible double-layer interaction and a greater distance of separation between particles. At constant ϕ_w, h increases with n and for $n = 3$, $h = 207$ nm; this distance at 10^{-4} M NaCl is about $7\kappa^{-1}$ where κ^{-1} is the Debye length and double-layer interactions are quite weak. These calculations suggest therefore that $1 < n < 3$ for this clay so that for $\phi_w = 0.05$, 0.06 and 0.07, distances of separation can occur within the range 33 nm to 144 nm depending on n.

As each particle rotates, the volume swept out produces interpenetration of electrical double layers over these distances. Double-layer forces thus restrict the motion of the particles and a disordered structure evolves. These forces of repulsion increase with reduction in ionic strength at constant ϕ_w and account for the increase in G_e below the ccc shown in Fig. 4.

Similar interactions occur between double layers with increasing solids concentration and the non-linear increase in the force of repulsion between layers with the decrease in h is reflected in the power law dependency of G_e on

ϕ (Fig. 6). This dependency is stronger ($m = 5.6$) than that reported by Callaghan and Ottewill [1] who found thus $E \sim \phi_w^{3.2}$ for sodium montmorillonite suspensions at 10^{-4} M NaCl where E is an elastic modulus obtained from compression cell measurements. This possibly reflects differing surface electrical properties of the two clays.

The nature of the interactions between particles and that of the structure which evolves in montmorillonite suspensions depends on pH (at constant ionic strength) and δ. Numerical solution of the two-dimensional non-linear Poisson–Boltzmann (PB) [5] in which a montmorillonite particle is modelled as a circular disk shows that when δ is small relative to the Debye length the negative double layer extending from the faces can spill over into the edge region and swamp any positive edge charge. The computations (using surface charge densities representative of montmorillonite clay) suggest that for $\delta = 1$ nm this will occur for $C \leq 5 \times 10^{-3}$ M NaCl. More recently Chang and Sposito [6] have given further numerical solutions of the PB equation for a 2:1 clay which show that the "spillover" effect can be much diminished with increasing thickness of disk. For a disk of radius 250 nm (similar to the present clay platelets) and $\delta \geq 3$ nm the positive field of the edge is less affected by the face double layer in the presence of 10^{-4} M NaCl.

If $\delta = 1$ nm the aforementioned calculations indicate that in 10^{-4} M NaCl and for pH < iep electrostatic f-e coagulation would not occur and a dispersive structure would be formed for $\phi > \phi_c$. Accordingly G_e should decline with increase in ionic strength. However, the results in Fig. 5 show that G_e increases with reduction in pH below about 5 in 10^{-4} M NaCl. Further the $G(t)$ data at pH < 5 (Fig. 3) exhibit the marked time dependency of cohesive structure with the rate of increase in G increasing with reduction in pH. A possible explanation is that the thickness of particles is such that the influence of face double layers is sufficiently reduced for f-e electrostatic attraction to occur. Within the proposed constraints for n this might be achieved with $n = 2$ so that each particle with an interposed layer of liquid would be about 3 nm thick. Thus f-e attraction increases with growing positive charge on the edge and provides an explanation of the increase in G_e with reduction in pH below 5. Below pH 4 this process would be assisted by the compression of face double layers as the ionic strength increases.

Near pH 6 the reduction in edge charge allows "spillover" of the face double layer to occur and G_e gradually increases with repulsion between similarly charged double layers until about pH 9. The decline in the modulus near pH 10 is attributed to the increase in ionic strength.

The results in Fig. 5 show that the wave rigidity modulus is strongly pH dependent at 5×10^{-2} M NaCl. At pH > iep the e-e interactions between particles weaken and G_e declines with evidence of a minimum near pH 8. At pH < iep the electrostatic f-e attraction is enhanced by van der Waals' attraction and accounts for the rise in G_e to a maximum near pH 3.8.

Conclusions

The investigation has shown that elastic properties of sodium montmorillonite suspensions in the presence of NaCl are satisfactorily accounted for in terms of cohesive and dispersive structures. Which structure evolves depends in a complex manner on pH and ionic strength. The results suggest that at low pH cohesion can be attributed to face-edge electrostatic attraction made possible in part by incomplete delamination of the clay.

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