Some Properties of Clay-Water Dispersions [and Discussion]

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Some properties of clay–water dispersions

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The bulk properties of clay–water dispersions, particularly with montmorillonites, depend on the very large surface area of the materials and their plate-like form. Owing to isomorphous substitution in the clay lattice the plates are charged and hence interact electrostatically with each other. The form of the interaction was tested using macroscopic clay surfaces in the form of cleaved mica and the results compared with those obtained by compression of concentrated aqueous dispersions of various montmorillonites in a homoionic form. The results obtained with mica and lithium montmorillonite were comparable suggesting the latter disperses as single plates. When sodium, potassium and caesium were used as the counter-ions for montmorillonite, differences were observed which were attributed to face–face association. The consequences of isomorphous substitution in either the tetrahedral or the octahedral layer were also examined.

1. INTRODUCTION

Naturally occurring clays owe many of their properties to the isomorphous substitution that occurs in the tetrahedral and octahedral layers during their geological formation (van Olphen 1963). The defects that this replacement leaves in the clay lattice lead to the formation of an electric charge at the clay–water interface and hence to an electrostatic potential difference between the clay surface and the solution phase, the so-called electrical double layer. Consequently, at distances of the order of a few tens of nanometres electrostatic interaction occurs between the clay plates and the electrostatic forces generated play a significant role in determining the properties of clay–water dispersions. The quantitative investigation of these electrostatic forces is therefore important in order to understand how they are influenced both by the nature of the clay and the electrolyte concentration of the dispersion medium.

The most direct method for the examination of electrostatic forces is to use macroscopic surfaces with an intervening layer of liquid between them, and in the present work, dedicated to the examination of clay–clay surface interactions, we have used cleaved mica in a specially constructed apparatus designed for the direct measurement of surface forces. With clay–water dispersions the pressure generated in a clay dispersion has been measured directly as a function of the distance of separation between the clay plates.

A direct comparison of the results obtained suggests that for well-dispersed clays such as homoionic lithium montmorillonite, the pressure measurements on the dispersions are directly comparable with the macroscopic measurements on mica. Evidence was obtained for significant electrostatic effects and with the dispersions this was found to depend on the nature of the isomorphous substitution. In the presence of counter-ions other than lithium, for example, sodium, potassium and caesium, a significant reduction in interaction occurred which appeared to be due to the formation of associated face-to-face units of clay particles.

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2. EXPERIMENTAL

Materials

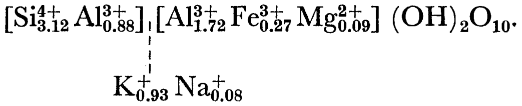
The distilled water used was doubly distilled from an all-Pyrex apparatus. All salts used were Analar grade materials.

The bentonite used was a sample of montmorillonite no. 26 from Clay Spur, Wyoming, as prepared for the American Petroleum Institute Clay Minerals Standards Project no. 49. It was converted into the homoionic form of lithium, sodium, potassium or caesium montmorillonite using the procedure previously described for the preparation of sodium montmorillonite (Barclay & Ottewill 1970; Callaghan & Ottewill 1974). Electron microscope examination of samples of lithium montmorillonite using the technique suggested by Greene *et al.* (1974) showed that it was dispersed essentially as single plates. The width and breadth of the plates however, varied over the range 0.2–0.7 μm. Hence although it appeared to be monodisperse with respect to plate thickness, the sample was polydisperse with respect to its face dimensions.

The sample of Cypern montmorillonite was kindly donated by Professor G. Lagaly of the University of Kiel as a dispersion of lithium clay in an electrolyte solution. It was reprocessed in concentrated lithium chloride solution to ensure conversion into the homoionic lithium form.

The sample of beidellite was kindly given to us by Professor A. Weiss of the University of Munich. The material was received in the dry state and was pinkish-white in colour. It was converted into the homoionic form using the procedure used previously for the preparation of sodium montmorillonite (Barclay & Ottewill 1970).

The mica used was from a sample of green mica. Lyons *et al.* (1981) have given a composition for this material as



$$\begin{array}{l}[\mathrm{Si}^{4+}_{3.12}\,\mathrm{Al}^{3+}_{0.88}]\,[\mathrm{Al}^{3+}_{1.72}\,\mathrm{Fe}^{3+}_{0.27}\,\mathrm{Mg}^{2+}_{0.09}]\,(\mathrm{OH})_2\mathrm{O}_{10}.\\ \qquad\qquad \mathrm{K}^{+}_{0.93}\,\mathrm{Na}^{+}_{0.08}\end{array}$$

Force measurements – macroscopic surfaces

These measurements were carried out using cleaved mica surfaces. The sheets of mica obtained were *ca.* 2 μm thick and were lightly silvered on the back surface; the latter was attached with adhesive to a hemi-cylindrical quartz former. Following the procedures of Tabor & Winterton (1969) and Israelachvili & Tabor (1972, 1973) this enabled a multiple beam interferometer (Tolansky 1948) to be used to determine the distance between the mica surfaces once they were immersed in electrolyte solution. The hemi-cylindrical surfaces were used in a crossed conformation. One of the formers, the uppermost, was attached to a transducer arm and the other, the lower, was attached to a micrometer with a very fine adjustment. Both mica surfaces were immersed in the electrolyte solution which was controlled at a temperature of 25 °C. The force of interaction was thus measured directly via the transducer and the distance of separation between the mica surfaces, in the electrolyte solution, by the multiple beam interferometer. A full description of this equipment will appear elsewhere (Lubetkin & Ottewill 1984).

Pressure measurements – clay dispersions

The apparatus used for the compression of the clay dispersions and for measuring its volume under a constant applied pressure has been described previously (Barclay & Ottewill 1970). In this equipment the clay particles were confined between a rubber membrane and a filter so arranged that the electrolyte expelled by the application of pressure was maintained in equilibrium with that of the dispersion. Under these conditions the total volume of the system was also maintained constant but the ratio of the volume of the clay dispersion to that of the electrolyte changed. A hydraulic system was used for the application of pressure and this allowed constant pressure to be accurately maintained. The stainless steel pressure cell, containing the clay dispersion, was immersed in a water bath maintained at a constant temperature of 25 °C.

3. Theory

The precise measurement of the force of interaction between surfaces, either for macroscopic surfaces or particle surfaces, requires that the internal force of interaction, F_I, should be balanced by an external applied force, F_E; if the force is applied per unit area of surface this gives the pressures P_I and P_E. It is required that P_E should be measurable by a physical technique, in the present case the transducer for macroscopic surfaces and the gauge pressure in the hydraulic system for the clay dispersions. The condition of equilibrium is illustrated schematically in figure 1 and for this condition we can write

$$P_I + P_E = 0.$$

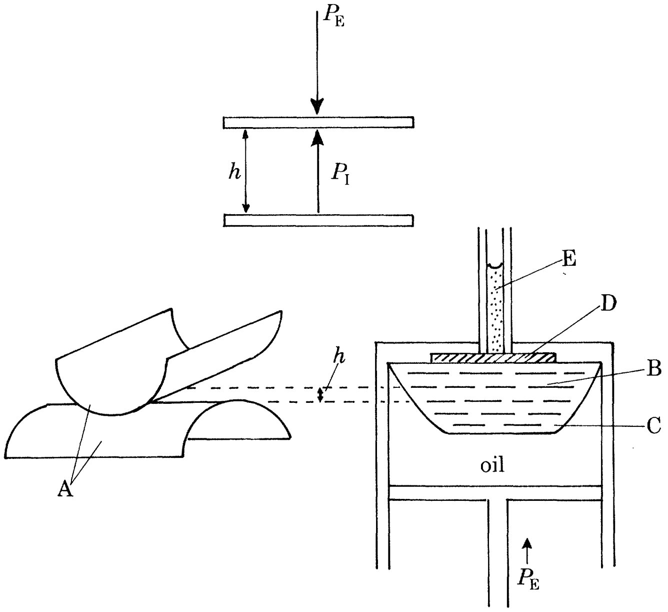


Figure 1. Schematic illustration of the balance of forces between plates and the apparatus used. A, mica surfaces; B, clay plates; C, rubber membrane; D, filter; E, dispersion medium.

The pressure P_I can be subdivided into various components and hence written in the form

$$P_I = P_{el} + P_A + P_B + P_{st} + P_{so},$$

where P_{el} = electrostatic pressure, P_A = the van der Waals attractive pressure, P_B = the Born repulsion, P_{st} = a steric effect due to adsorbed molecules and P_{so} = a solvation pressure.

In this work we concentrated on long range interactions and chose conditions such that P_{el} is the dominant term. This is justified by the fact that P_B and P_{so} appear to be very short range terms and calculation shows P_A to be very small for the conditions used. In the absence of added macromolecules we will assume that $P_{st} = 0$ also.

It was shown by Langmuir (1938) that the electrostatic repulsive pressure for two flat plates both having the same surface potential ψ_s was given by,

$$P_{el} = 2n_0kT(\cosh u - 1), \tag{1}$$

where n_0 = the number of ions per unit volume (m^3) in the bulk electrolyte phase, k = the Boltzmann constant, T = absolute temperature, and u for 1:1 electrolytes is given by

$$u = e\psi_d/kT, \tag{2}$$

where e = the fundamental unit of charge and ψ_d = the electrostatic potential at a distance midway between the plates, and at a distance d from the surface of each plate. The surface to surface distance between the plates, h, is thus given by

$$h = 2d. \tag{3}$$

For the interaction of diffuse electrical double layers for flat surfaces at constant surface potential, ψ_s, the distance h is given by (Verwey & Overbeek 1948).

$$h = -\frac{2}{\kappa}\int_z^u \frac{\mathrm{d}y}{[2(\cosh y - \cosh u)]^{\frac{1}{2}}} \tag{4}$$

with $z = e\psi_s/kT$ and $y = e\psi/kT$, the general variable. κ for 1:1 electrolytes is given by,

$$\kappa^2 = 2n_0e^2/\epsilon_r\epsilon_0kT \tag{5}$$

with ϵ_r = the relative permittivity of the solution phase and ϵ_0 that of free space.

For long range interaction defined by the condition that $h > 2/\kappa$, we find the equation,

$$P_{el} = 64n_0kT\tanh^2\left(\frac{e\psi_s}{kT}\right)\exp(-\kappa h) \tag{6}$$

or

$$\ln P_{el} = \ln\left[64n_0kT\tanh^2\left(\frac{e\psi_s}{kT}\right)\right] - \kappa h \tag{7}$$

so that for long distances of separation it can be anticipated that curves of $\ln P_{el}$ against h should be linear. Furthermore the negative slope should yield a value of κ and the intercept at $h = 0$ a value of the surface potential ψ_s.

In this work the surface potential ψ_s has been taken as the diffuse layer potential, and hence it has been assumed that it is close to the Stern potential. Detailed arguments about the inner part of the double layer will not be considered.

The geometry of crossed cylinders used in the case of the mica experiments is equivalent in interaction terms to interaction between a flat surface and a sphere of radius R. This gives, again for the condition $h > 2/\kappa$, the equation,

$$\ln\left(\frac{F_{el}}{2\pi R}\right) = \ln\left[\frac{64n_0kT}{\kappa}.\tanh^2\left(\frac{e\psi_s}{kT}\right)\right] - \kappa h, \tag{8}$$

where F_{el} = the electrostatic force between the sphere and the plate. Thus (8) can be compared with (7). R was taken as the radius of the hemi-cylinder.

The significance of h in the two systems is illustrated in figure 1.

4. Results

Mica surfaces

Figure 2 shows the curves of lg $(F/2\pi R)$ against h obtained using mica surfaces in solutions of potassium chloride at concentrations of 10^{-2} and 10^{-3} mol dm^{-3}. F was taken as the force of repulsion measured directly using the transducer arrangement. As can be seen from the figure the range of the electrostatic forces is much greater in 10^{-3} mol dm^{-3} potassium chloride than in 10^{-2} mol dm^{-3} potassium chloride. For the range of distances shown in figure 2 good linear plots of lg $(F/2\pi R)$ against h were obtained. In 10^{-3} mol dm^{-3} potassium chloride solution an experimental value of 9.6 nm was obtained for κ using (8) which compares favourably with the theoretical calculation of 9.62 nm from (5). A value of 84 mV was obtained for $|\psi_s|$ from the intercept at $h = 0$ and (8). In 10^{-2} mol dm^{-3} potassium chloride solutions an experimental value of 3.5 nm was obtained for κ compared with the theoretical value of 3.04 nm. The value of $|\psi_s|$ obtained was 79 mV. These values of $|\psi_s|$ are comparable with the values of ζ-potential obtained by Lyons *et al.* (1981) using the streaming potential technique on freshly cleaved sheets of green mica.

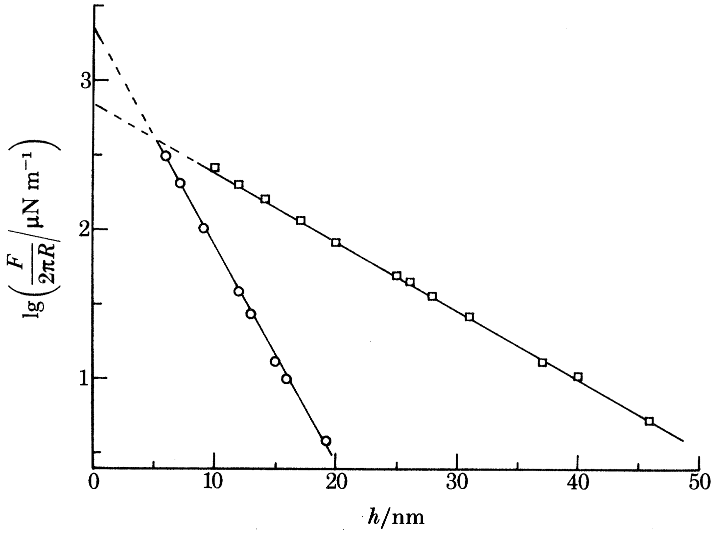
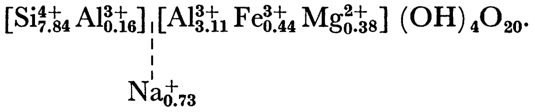


Figure 2. Lg $(F/2\pi R)$ against h for mica surfaces in, —○—, 10^{-2} mol dm^{-3} potassium chloride; —□—, 10^{-3} mol dm^{-3} potassium chloride.

These results show that at long distances, the forces of electrostatic repulsion appear to be the dominant forces and that these can be explained using the theory of the electrical double layer for the condition that $h > 2/\kappa$.

Wyoming bentonite

The sample used was found by analysis of the sodium form and using the procedure of Marshall (1949) to have the composition,



$$[\mathrm{Si}^{4+}_{7.84}\,\mathrm{Al}^{3+}_{0.16}]\,[\mathrm{Al}^{3+}_{3.11}\,\mathrm{Fe}^{3+}_{0.44}\,\mathrm{Mg}^{2+}_{0.38}]\,(\mathrm{OH})_4\mathrm{O}_{20}.\quad \mathrm{Na}^{+}_{0.73}$$

Hence the isomorphous substitution was primarily in the octahedral layer. This gave a cation exchange capacity of 0.91 meq g^{-1} and a surface charge density (σ) of 11.6 μC cm^{-2}.

The compression curves obtained using samples of lithium montmorillonite are shown in figure 3 in the form of lg P against V/m, where V = the volume of the clay dispersion and m the mass of clay contained in it. As explained in previous work the first compression on the clay dispersion rearranges the plates into an ordered parallel array (Barclay & Ottewill 1970; Callaghan & Ottewill 1974). Once this has occurred subsequent compression and decompression curves are very reproducible. Consequently, the results given in this work are the second compression runs.

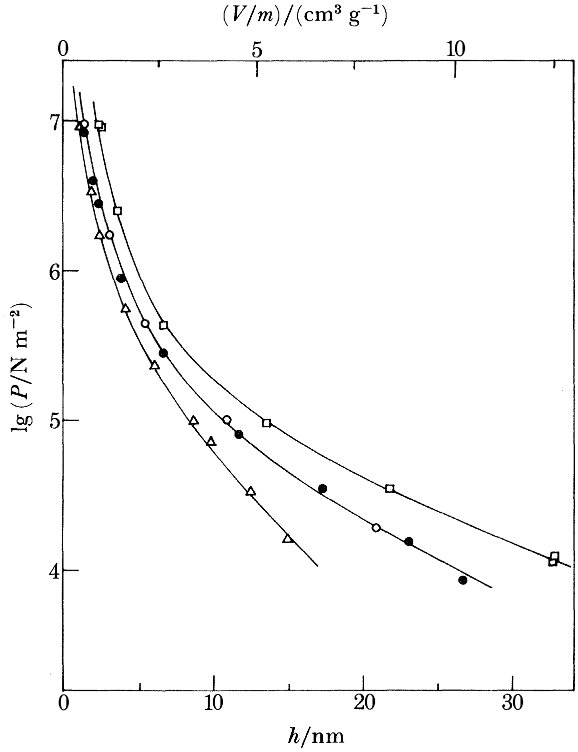


FIGURE 3. Lg P against V/m (and h) for lithium Wyoming bentonite in lithium chloride solutions. □—□, 10^{-4} mol dm^{-3}; ●—●, 10^{-3} mol dm^{-3}; ○—○, 10^{-3} mol dm^{-3} (centrifuged sample); △—△, 10^{-2} mol dm^{-3}.

For a material, such as a montmorillonite clay, essentially all the surface area is that due to the faces of the plates and for this situation the plate surface to surface separation, h, is given by the expression,

$$h = 2V/mA, \tag{9}$$

where A = the specific surface area of the clay. For lithium montmorillonite this was found to be 763 m^2 g^{-1}. The use of this expression has been checked using both small angle X-ray diffraction (Barclay & Ottewill 1970) and small angle neutron diffraction (Cebula & Ottewill 1981) and good agreement between experiment and values of h calculated from (9) obtained. Moreover, neutron scattering studies on compressed lithium montmorillonite samples (Cebula *et al.* 1979) have confirmed that the plate arrangements are essentially parallel although some grain boundaries occur owing to the polydispersity in the face dimensions of the plates.

By the use of (9) it is possible to convert the values of V/m into values of h and the results plotted in the form, lg P against h are shown in figure 3 for three different electrolyte concentrations, 10^{-4}, 10^{-3} and 10^{-2} mol dm^{-3} lithium chloride. As in the case of the mica surfaces the effect of electrolyte concentration on the electrostatic forces is discernible and the long range nature of the interactions, particularly in 10^{-4} mol dm^{-3} lithium chloride is clearly apparent.

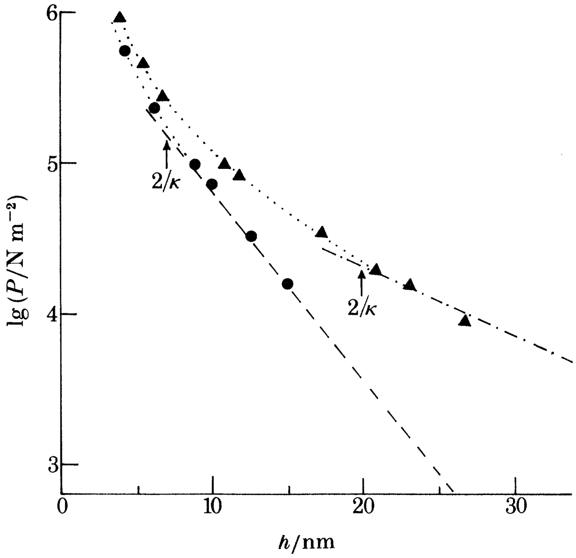


FIGURE 4. Lg P against h for Wyoming bentonite in lithium chloride solutions. ▲—▲, 10^{-3} mol dm^{-3}; ●—●, 10^{-2} mol dm^{-3}; – – –, calculated from simple electrostatic model.

In figure 4 the results obtained for the lithium bentonite are compared with the calculated curves of lg P_{el} against h for h values greater than $2/\kappa$ where (7) is valid. Good agreement is obtained between the calculated and experimental values of κ as shown by the dashed line. The estimated value of $|\psi_{\text{s}}|$ is of the order of 250 mV in 10^{-3} mol dm^{-3} lithium chloride solution and 150 mV in 10^{-2} mol dm^{-3} solution. These results strongly suggest that the lithium montmorillonite is well dispersed into single plates and that the h distances are essentially correct. Confirmation of the well dispersed state of the lithium montmorillonite was obtained from electron microscopy and from small angle neutron scattering studies (Cebula & Ottewill 1981; Cebula *et al.* 1980).

The compression results obtained on homoionic potassium Wyoming bentonite are given in figure 5 for electrolyte concentrations of 10^{-4}, 10^{-3} and 10^{-2} mol dm^{-3} potassium chloride. It is clear from these data that for the same interaction pressure the distance between the plates is apparently substantially decreased. It was also noted that there was a change in the optical characteristics of the samples in that they appeared somewhat whiter in colour. This suggests the formation of associated units. Electron microscopy also indicated that there appeared to be face–face association of the montmorillonite plates in the presence of potassium. However, the degree of association appears to be small and the evidence suggests that only a few units are involved in the stack. Greater binding of the potassium ions to the clay surface would be anticipated on the basis of the greater polarizability of the K^{+} ion compared to the Li^{+} ion.

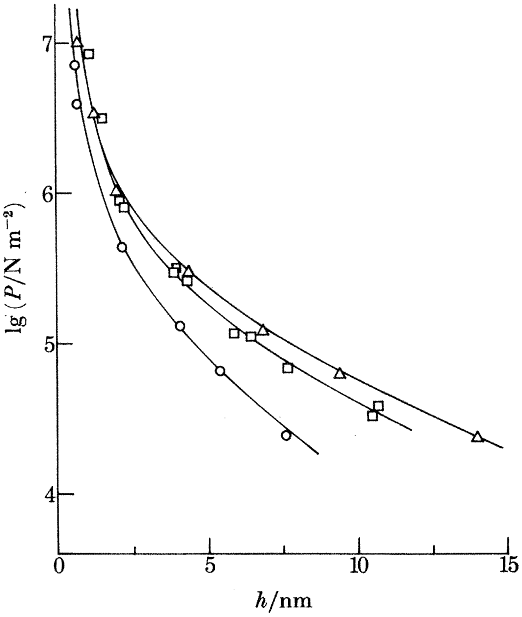


FIGURE 5. Lg P against h for Wyoming bentonite in potassium chloride solutions. △—△, 10^{-4} mol dm^{-3}; □—□, 10^{-3} mol dm^{-3}; ○—○, 10^{-2} mol dm^{-3}.

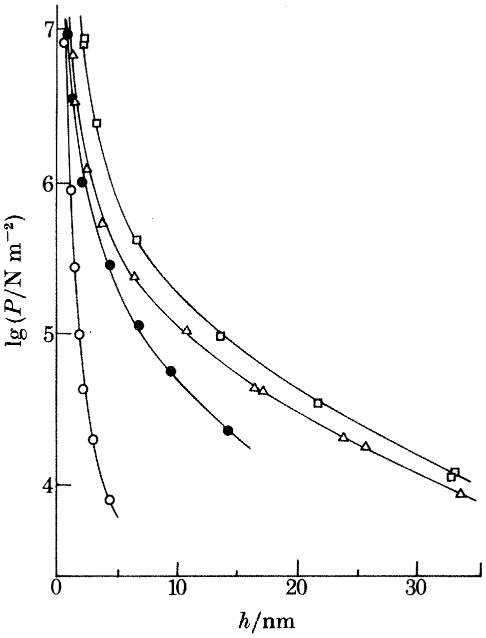


FIGURE 6. Lg P against h for Wyoming bentonite in 10^{-4} mol dm^{-3} salt solutions of various counter-ions. □—□, Li^+; △—△, Na^+; ●—●, K^+; ○—○, Cs^+.

As anticipated this effect becomes more pronounced in the presence of Cs^+ ions and figure 6 gives a comparison of the results obtained at an electrolyte concentration of 10^{-4} mol dm^{-3} with homoionic lithium, sodium, potassium and caesium Wyoming bentonites. Again the optical appearance of the caesium samples was quite different from that of the lithium samples in that they were much whiter in appearance. This again suggested the formation of stacks of montmorillonite plates in the presence of caesium ions in addition to the more pronounced binding of the Cs^+ ions to the clay surface.

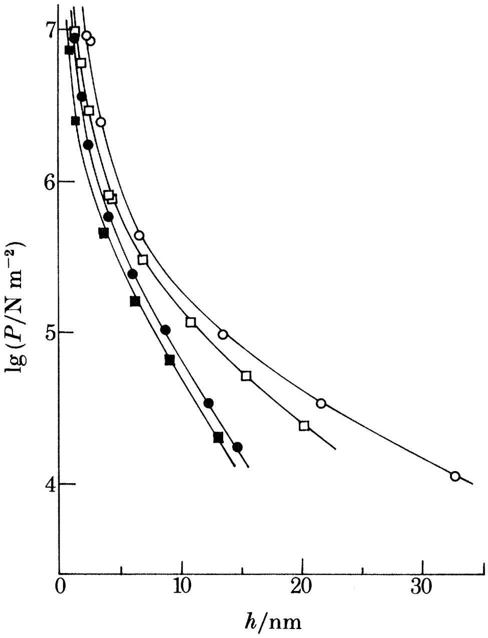
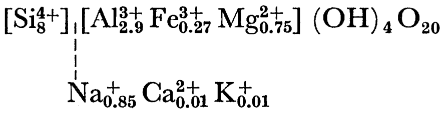


FIGURE 7. Lg P against h for clay dispersions in 10^{-4} mol dm^{-3} lithium chloride solutions. ○—○, Wyoming bentonite; □—□, Cypern montmorillonite. Filled symbols: results in 10^{-2} mol dm^{-3} lithium chloride solutions.

Cypern montmorillonite

The material used was found to have the composition



$$\underset{Na^{+}_{0.85}\,Ca^{2+}_{0.01}\,K^{+}_{0.01}}{[Si^{4+}_{8}]\,[Al^{3+}_{2.9}\,Fe^{3+}_{0.27}\,Mg^{2+}_{0.75}]}\,(OH)_4\,O_{20}$$

as originally obtained and hence had no isomorphous substitution in the tetrahedral layers. It was converted by the procedures described into the homoionic lithium form and the compressibility examined in 10^{-4} and 10^{-2} mol dm^{-3} lithium chloride solutions. The results obtained are presented in figure 7 as curves of lg P against h and compared with the results for Wyoming bentonite. At the same distances of plate separation the pressures exerted by the Cypern montmorillonite are significantly lower than those found using Wyoming bentonite. The surface charge density of the Cypern montmorillonite was found to be 10.3 μC cm^{-2} with a cation exchange capacity of 0.81 meq g^{-1} and hence was lower than that for the bentonite.

The results for the Cypern material can be compared with those of the bentonite at the values of $h > 2/\kappa$ in 10^{-2} mol dm^{-3} lithium chloride when it becomes clear that the slopes in this region are essentially identical. The intercept obtained by extrapolation at $h = 0$ is however lower for the Cypern material and using this value an estimate is obtained for the surface potential of 113 mV compared to 150 mV for the bentonite.

It is also noticeable that for the Cypern material the distance of closest approach of the plates at the highest pressures measured is 1.3 nm in 10^{-4} mol dm^{-3} lithium chloride whereas for the bentonite it is *ca.* 2.2 nm. Presumably this is also an effect of the lower surface charge density.

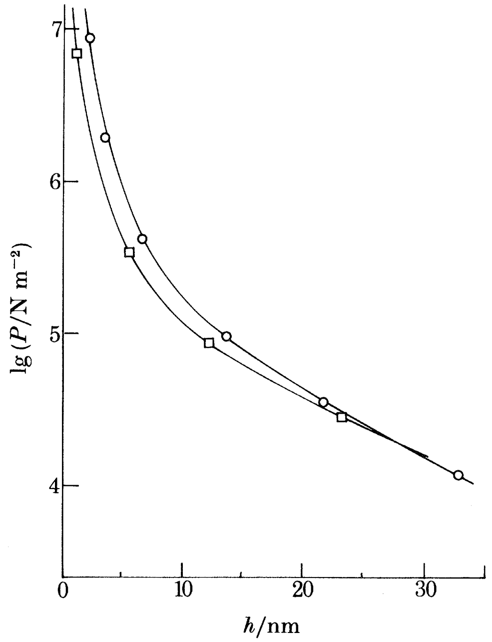
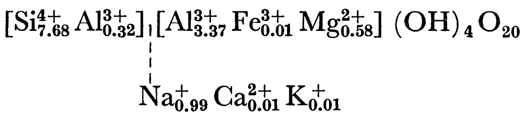


FIGURE 8. Lg P against h for clay dispersions in 10^{-4} mol dm^{-3} lithium chloride solutions. ○—○, Wyoming bentonite; □—□, beidellite.

Beidellite

The material used was found to have the composition,



$$[\mathrm{Si}^{4+}_{7.68}\,\mathrm{Al}^{3+}_{0.32}]\,[\mathrm{Al}^{3+}_{3.37}\,\mathrm{Fe}^{3+}_{0.01}\,\mathrm{Mg}^{2+}_{0.58}]\,(\mathrm{OH})_4\,\mathrm{O}_{20}$$

$$\mathrm{Na}^{+}_{0.99}\,\mathrm{Ca}^{2+}_{0.01}\,\mathrm{K}^{+}_{0.01}$$

in the original form. It was converted into the homoionic lithium form by the same procedure as that used for the other clays. However, for this material a substantial amount of isomorphous substitution was present in the tetrahedral layer and it had the highest surface charge density of the clays examined, 13.5 μC cm^{-2}. The cation exchange capacity was 1.06 meq g^{-1}.

The curve of lg P against h obtained for the beidellite dispersed in 10^{-4} mol dm^{-3} lithium chloride is given in figure 8. The form of the curve is interesting in that when it is compared with the results for lithium bentonite there appears to be a cross-over at large separations. This, in principle, would indicate a lower surface potential at the beidellite–water interface than at the montmorillonite interface. The inference from this is that the deficit of charge in the tetrahedral layer causes a much stronger binding of Li$^+$ ions to the surface than occurs with montmorillonite.

In this context it is also significant that at the highest pressures examined the beidellite plates approach much more closely than the montmorillonite plates under comparable conditions; this also could be a consequence of tighter counter-ion binding.

5. Discussion

The direct measurements of electrostatic interaction forces between mica surfaces and between plates of lithium montmorillonite (bentonite) indicate that the dominant interaction forces are electrostatic in nature. By using the simple theory of electrostatic interaction embodied in (7) and (8) good agreement is obtained between experiment and theory for the condition $h > 2/\kappa$. The similarity of behaviour between mica surfaces and the lithium clays seems to provide strong evidence for the fact that the clay is dispersed as essentially single platelets. Small angle neutron scattering experiments by Cebula *et al.* (1980) on dilute dispersions of the same material also support this conclusion.

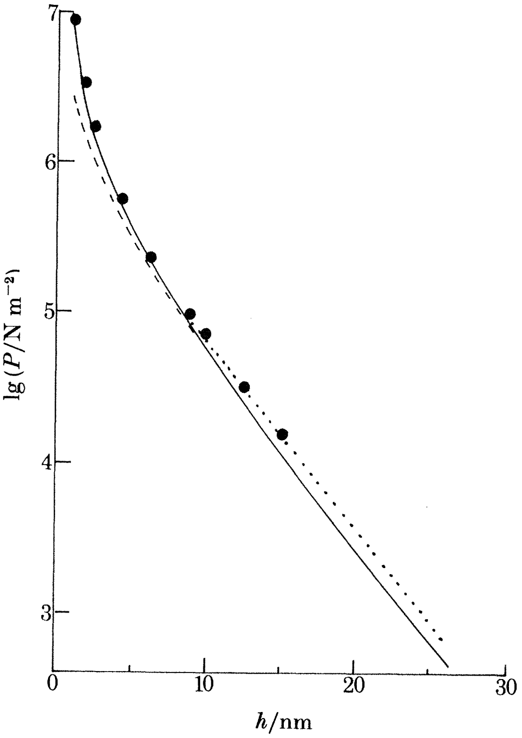


FIGURE 9. Lg P against h. ●—●, experimental data for lithium Wyoming bentonite in 10^{-2} mol dm^{-3} lithium chloride solution. – – –, constant potential model; ——, constant surface charge model: · · · · · approximate equation (7).

At the closer distances of approach of the lithium clays, when $h < 2/\kappa$, then the simple theory can no longer be expected to hold and the full theory given by (4) has to be used to give a comparison with the experimental data. Taking the lithium bentonite results in 10^{-2} mol dm^{-3} and using $\psi_s = 150$ mV, the value found for large distances from the simple theory, we obtain $z = 6$. Using the tabulations given by Verwey & Overbeek (1948) for interaction at constant potential this gave the curve of lg P against h shown as a dashed line in figure 9. Although the curve deviates from linearity at the closer distances and curves upwards, it falls below the experimental points.

However, since the electrostatic charge on clay surfaces arises as a consequence of isomorphous substitution in the lattice, it would appear physically more realistic to consider the interaction to occur at constant charge. This condition is satisfied by the equation

$$(2\cosh z - 2\cosh u)^{\frac{1}{2}} = \sigma\left(\frac{1}{2\epsilon_r \epsilon_0 n_0 kT}\right)^{\frac{1}{2}}, \tag{10}$$

where the right-hand side is a constant determined by the magnitude of the surface charge density. As $h \to \infty$ then $u \to 0$ and z has the same value as for interaction at constant potential. Hence taking $z = 6$ the constant charge curve of lg P against h was calculated for 10^{-2} mol dm^{-3} lithium chloride. The result is shown as the continuous line in figure 9. At the longer distances, as anticipated, it is identical to the curve obtained at constant potential. At the shorter distances, however, it curves upward more strongly and lies very close to the experimental results. The value obtained for σ was 11.8 μC cm^{-2} which was remarkably close to the value obtained from the cation exchange capacity. Although the agreement between experiment and theory is good it must be treated with caution. The theory, for example, does not take into account such factors as the finite size of the ions and it would be anticipated that this should be very important at close distances.

An interesting point is that at the longer distances the approximate theory, (7), appears to give a better fit to the experimental data than the more exact one. This may, however, be because the approximate theory slightly underestimates the surface potential.

A point of major interest is the fact that for counter-ions other than lithium the properties of the bulk clay–water mixtures deviate from that expected on the basis of electrostatic interaction with the deviation being the most pronounced in the case of the caesium clay. This is demonstrated clearly in the results presented in figure 6. It was also found (Middleton 1978) that the samples had different optical properties; the lithium and sodium bentonite dispersions were yellow whereas a dispersion of caesium bentonite was creamy white in appearance. The potassium bentonite was intermediate in colour between the lithium and caesium dispersions. The intensity of light scattered by the dispersions was greatest for the caesium dispersions. These results suggested some association between the plates. From small angle neutron scattering measurements, Cebula *et al.* (1980) using dilute dispersions of the same bentonite suggested that in potassium bentonite dispersions the average unit consisted of a pair of platelets with two molecular layers of water between them and in the case of caesium bentonite the associated unit consisted of three platelets interleaved with double layers of water. It is of interest from this point of view that the distances between the plates at the highest pressures (figure 6) are closely similar for the potassium and caesium clays and tend to a limiting value of *ca.* 0.7 nm which is close to the value found by Cebula *et al.* (1980). It would appear, therefore, that the changes in the lg P against h curves found by changing counter-ions can be explained by the formation of associated units. The explanation of this association phenomenon is not clear but is most likely connected with the order of the energy of ion-binding to the clay surface, in this case in decreasing binding order

$$\mathrm{Cs^+ > K^+ > Na^+ > Li^+}.$$

Consistent with this explanation are the results obtained with Cypern montmorillonite and beidellite. In the former case comparison of the lithium form with lithium bentonite indicated that the pressures at the same distance of separation were lower for the Cypern material.

This seemed to be consistent with the lower surface charge density of 10.3 μC cm^{-2} which on figure 9 would shift the curves closer to the ordinate. The beidellite on the other hand had a much higher surface charge density and yet the pressure curve obtained with the lithium form crosses the curve for the lithium bentonite at longer distances and has a smaller slope which suggests a smaller surface potential than the beidellite. At higher pressures the plates move more closely together than those of lithium bentonite. A tentative explanation of these effects is that the isomorphous substitution in the tetrahedral layer in the case of the beidellite causes a much stronger ion binding of the Li$^+$ ion to the surface than occurs with the bentonite where the substitution is primarily in the octahedral layer.

One of the properties of clay–water systems which is important in their use is their ability to form gels or to exhibit elastic properties. If we use the bulk modulus as defined by

$$E = V\left(\frac{\mathrm{d}P}{\mathrm{d}V}\right)_T$$

it is immediately clear that for a *highly aligned* system of plates as apparently given by the lithium clays used in this work we can define the elastic modulus as

$$E = h\left(\frac{\mathrm{d}p}{\mathrm{d}H}\right)_T$$

and hence directly relate the modulus to the pressure against distance curves. As we pointed out in our previous work (Callaghan & Ottewill 1974) this suggests that the gel properties of well-dispersed montmorillonite plates should be directly related to the electrostatic interactions between them, an idea originally introduced by Norrish (1954). Evidence for the importance of this type of interaction in dispersions of sodium montmorillonite has also been found by Rand *et al.* (1980). We conclude therefore from our observations that the elastic modulus of lithium montmorillonite should be strongly dependent on lithium chloride concentration and that in the case of caesium montmorillonites, where plate–plate association occurs, the onset of elastic gel properties should occur at higher concentration of clay than required with lithium clay at the same homionic salt concentrations.

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Discussion

P. Barnes (*Department of Crystallography, Birkbeck College, Malet Street, London WC1E 7HX, U.K.*). The precision force–distance apparatus described by Professor Ottewill appears to resemble the design of Israelachvili *et al.* (Canberra, Australia) who has also studied mica–mica properties in various solutions. My memory of that system is that it depends for its success on having molecularly smooth crossed cylinders. This requirement would seem to restrict clay material usage to near perfect mica.

R. H. Ottewill. The direct measurement of interaction forces is restricted to using very smooth surfaces. The crossed-cylinder conformation that we used is similar to that originally used by Tabor & Winterton (1969) and in the subsequent studies by Israelachvili (for example, 1973 and 1978). The method of force measurement in our equipment, however, is different in design from that of Israelachvili and can be used for both kinetic measurements and constant force measurements. Our interest was essentially to compare direct measurements of force between single macroscopic surfaces with the pressures measured on assemblies of clay plates. The results obtained with lithium montmorillonite give us some confidence that the two can be related and that the compression technique can be used to obtain information about clay–water dispersions.

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P. Nadeau (*The Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen AB9 2QJ, U.K.*). I would like to say that transmission electron microscopy and X-ray diffraction results obtained at the Macaulay Institute confirm the presence of elementary smectite layers in suspension. The achievement of complete dispersion of the clay is related not only to the exchangeable cation, but also to the use of dialysis to ensure quantitative retention of the finely dispersed material during final washings, and to the removal of incompletely dispersed aggregates by centrifugation. Another factor of importance is the concentration of clay material in the final suspension.

R. H. Ottewill. I agree with your comments. In our work, in the preparation of the homoionic clays, a number of dialysis stages were used, each followed by sedimentation to remove extraneous material. In the case of lithium montmorillonite, using cytochrome *c*-coated carbon grids as the substrate, single plates of clay were visible in transmission electron microscopy. In the case of caesium montmorillonite stacks of plates were common. It is certainly probable that the formation of tactoids is both clay concentration and electrolyte concentration dependent. This information should, in principle, be derivable from the compression curves given in the paper.

J. Fripiat (*C.N.R.S., C.R.S.O.C.I., 1B rue de la Férollerie*, 45045, *Orleans, Cedex, France*). In his talk Professor Ottewill related the swelling pressure to the water/clay ratio. Then the water/clay ratio was transformed into an average distance between clay sheets by assuming the complete availability of the interlayer surface area (*ca.* 800 $m^2 g^{-1}$) in agreement with Low & Oliphant (1982). It was shown that the swelling pressure can be predicted by the double layer theory for ratios higher than 10.

The procedure for calculating the average distance implies that infinite swelling occurs in dilute clay suspensions at low ionic strength.

This conception contradicts observations reported by Fripiat (this symposium) which lead to the conclusion that even under these extreme conditions, tactoids are formed and that these tactoids must be considered as 'textural units' from which the suspension is made. This conclusion came from the good agreement between heats of immersion and nuclear magnetic resonance relaxation time measurements which, in case of swelling silicates, shows that the surface available to water is about an order of magnitude less than the total (internal and external) surface area.

Ottewill has used, among others, Li and Na-Wyoming bentonites, whereas Fripiat studied Na and Ca-hectorites or Na-laponite but it seems rather improbable that the 10-fold difference can be explained by differences in clay compositions or morphology, or both.

There is thus an important disagreement between the approaches followed in these two contributions which deserves further study, particularly because they are important in many situations where the aggregation of clay particles is important (drilling muds, soil mechanics and so on).

Suppose, that only limited swelling occurs so that the intersheet distance never permits a fast exchange between interlayer water and bulk water. There may be an equilibrium between tactoids and individual sheets in the suspension but it should be strongly displaced in favour of the tactoids. As a first approximation let us assume that more than 80% of the sheets never expand for more than 2 nm (basal spacing about 3 nm). What would be the consequence in adopting such a model, which is strongly supported by two independent techniques (heats of immersion and n.m.r.) on the calculation of swelling pressures as carried out by Ottewill?

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R. H. Ottewill. Thank you for your very interesting comments which are well taken.

In the case of lithium montmorillonite, thoroughly ion-exchanged over a substantial period of time, with frequent sedimentation stages to remove extraneous material, we are pretty certain that with Wyoming bentonite we do obtain a very well dispersed material. In the pressure measurements we also started with a very dilute dispersion, *ca.* 2% (by mass), and obtained alignment of the plates by successive compressions and decompressions. Determination of the interplate spacing by X-ray diffraction and neutron diffraction over a very wide concentration range gave distances that were within a small percentage of those calculated using the surface area of the clay as 763 $m^2 g^{-1}$. Moreover, as mentioned in my reply to Dr Nadeau transmission electron micrographs of lithium montmorillonite, using cytochrome *c*-coated carbon grids, showed the material to be essentially all single plates. In addition the compression measurements with lithium montmorillonite and their agreement with the theory of diffuse double layer interaction suggests that the plates are well dispersed. Clearly, however, there must be some 'grain boundaries' in the arrangement of the plates in the cell as a consequence of the polydispersity in the face areas of the plates. If tactoids do exist in aqueous dispersions of lithium montmorillonite I think it must be to a very small extent. It would be nice to check this by your n.m.r. technique but I think this would be difficult owing to the presence of isomorphously substituted Fe^{3+} in the lattice.

In the case of sodium, potassium and caesium montmorillonites we would certainly concur that tactoid formation occurs. In the case of caesium samples this is visible from the optical properties. The changes in the compression curves with the nature of the counter-ion can also be explained by face–face association with the counter-ions held between the plates. I have not attempted to put this on a quantitative basis but the question you have put has stimulated me to attempt this. The measurements with sodium montmorillonite would indicate a small extent of tactoid formation. This becomes more pronounced with potassium as the counter-ion and even more pronounced with caesium. This order of effect is confirmed by the small angle neutron scattering studies of Cebula *et al.* (1980) on dilute dispersions of the same materials.

I agree that there is an important point here in the difference between the methods, although the measurements have been made on different materials, which should be cleared up. I hope that in the near future we can pursue the matter further.

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