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VERMICULITE AS A MODEL SYSTEM IN THE TESTING OF DOUBLE LAYER THEORY

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Abstract—The microelectrophoretic and adsorption behaviour of lithium vermiculite has been studied as a function of lithium chloride concentration. This was done in an attempt to establish the applicability of such systems to the testing of theories of interaction of flat plates, and in so doing to throw further light on swelling measurements performed on such materials. The studied behaviour, while highly unusual, gave quite good agreement between adsorption and microelectrophoretic parameters and agreed, qualitatively, with some earlier measurements on similar materials.

The observed properties appear to be due to some rather specific structuring effects, either of the oxide surface or of the electrolyte ions. If this is so, these systems are far from ideal models for the testing of the theory of interaction of two uniform flat plates.

INTRODUCTION

THE WELL known and generally accepted theory for the stability of lyophobic colloids of Deryaguin, Landau, Verwey and Overbeek (D.L.V.O.) (e.g. Verwey and Overbeek, 1948) considers particle interactions for two geometrically-simple systems: (i) the interaction between infinite flat plates and (ii) the interaction between finite spheres. In practice of course, particles in most real systems are neither flat plates nor perfect spheres. Depending on the size, shape and ionic environment of specific particles, one of the above two conditions is assumed to apply, and in experiments designed to test the theories conditions are generally chosen such that the errors involved in such an assumption are small.

For any rigorous testing of the theory, however, it is desirable that large flat plates and/or uniform spheres be used. Polymer science can provide us with the latter as the preparation and use of monodisperse latexes of, for example, polystyrene is, by now, quite widely documented. One can, with varying degrees of difficulty, prepare spherical latex particles of any desired diameter up to *ca.* *10 μ* and with a range of surface charge densities. Adsorption of charged surface active species can be used to adjust the surface charge to any desired value.

Nature, on the other hand, appears to provide us with a very close approximation to an infinite uniform flat plate, in the alumino-silicate clay minerals. A small number of the 2 : 1 layer alumino-silicates display the interesting property of macroscopic swelling (Garrett and Walker, 1962). The equilibrium separation between the primary sheets of these materials, which varies as a function of solution ionic strength, occurs when the resultant of the forces on the plates is zero. The two main forces here are the electro static repulsion and van der Waals or dispersive attraction. Comparison of a theoretical equilibrium separation, calculated from the D.L.V.O. theory, with an experimental separation, measured by low-angle X-ray diffraction (Norrish, 1954) affords a test of the theory.

The two commonly used 2:1 layer alumino-silicates are vermiculite and montmorillonite, the latter being the first to be subjected to swelling measurements (Norrish, 1954). The structure of these clays is such that by isomorphous substitution either of Al^{3+} for Si^{4+} in the silica tetrahedra or of Mg^{2+} for Al^{3+} in the alumina octahedra the sheet acquires an overall negative charge. There can be complicating effects such as positively charged edges (i.e. oppositely charged to the faces) caused by rupture of the aluinina. This overall negative charge is balanced by cations which reside between the primary silicate sheets. At sufficiently high electrolyte concentrations the sheets are very close together (~ 10–15 Å apart) and the Coulombic interaction between the sheets and the interlayer ions prevents swelling.

This is the "crystalline" region, which Norrish (1954) suggested would persist so long as the hydration energy of the cation and the osmotic effect of the water in the external solution was insufficient to overcome the electrostatic attraction.

As the electrolyte concentration is lowered a point is reached, depending on the nature of the adsorbed cation, at which a sudden "explosive" increase in X-ray spacing occurs (Fig. 1) and from this point on the spacing increases regularly with decrease in electrolyte concentration. Assuming that this low concentration swelling region (known as the region of double layer swelling) is governed by the attraction and repulsion forces which are invoked in the D.L.V.O. theory gives a very poor agreement between the theoretical calculations and the experimentally measured separations; the measured spacings are found to be considerably smaller than the theory predicts. Such behaviour could be due to either an increased attractive interaction or a reduced repulsive interaction but a number of lines of investigation suggest it is the former. Firstly, the theoretical calculations of Levine and Bell (1966) and, earlier, of Bolt (1955) suggest that the Gouy–Chapman description of the electrostatic repulsion is not likely to be greatly in error. Secondly, it is possible to examine the swelling under an imposed external pressure so that spacings remain very much smaller and the van der Waals attraction makes a negligible contribution to the balance of forces. Under these conditions, Warkentin and Schofield (1960) and Norrish and Rausell-Colom (1963) have shown that the relation between repulsion forces and distance is given very closely by the D.L.V.O. equation.

The commonly accepted explanation for the low spacings was provided by van Olphen (1962) who suggested that some of the montmorillonite particles are not exactly horizontally aligned and these interact by an edge-to-face Coulombic mechanism with other sheets in the stack, reducing its ability to swell. Contributions of such additional interactions to bulk suspension properties were discussed at length by van Olphen, who suggested that the effect would be reduced by addition of polyphosphate ion to reverse the sign of the positive clay plate edges. That such treatment did in fact reduce the attractive interaction was shown by Norrish and Rausell-Colom for montmorillonite (1963).

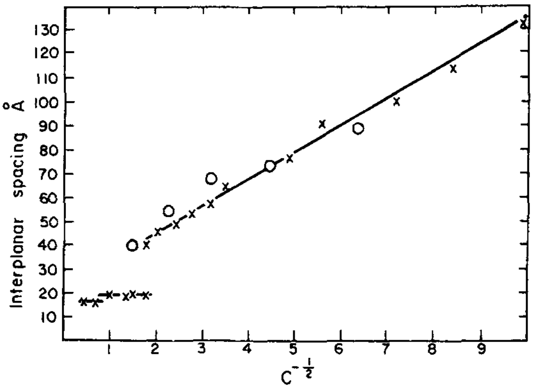

Fig. 1. The lattice expansion of montmorillonite as a function of electrolyte concentration (Norrish, 1954).

More recently, Norrish (1963), Rausell-Colom (1963–1964) and Garrett and Walker (1962), have investigated the swelling behaviour of vermiculite with counter-ions such as lithium and butylammonium. Vermiculite has the advantage over montmorillonite of occurring as much larger crystals with large axial ratios. This reduces significantly the possibility that an extra attractive force will be caused by edge-to-face interaction between sheets intercalated into a card-house type of structure. Here again it was found that agreement between predicted and measured spacings was rather poor, although Rausell-Colom (1964), by invoking specific adsorption of butylammonium ion, improved the agreement somewhat.

The literature gave no evidence of mobility measurements on the materials subjected to swelling measurements. It was, therefore, decided to subject these materials to micro-electrophoretic examination in an attempt to perhaps elucidate some of the peculiarities. The systems chosen were lithium and butylammonium vermiculites and their mobilities were studied over a concentration range similar to that used for the swelling measurements in an attempt to relate the two sets of data. It was intended that equilibrium spacings would be calculated from the mobility values and compared with those from the swelling work. It was also intended that adsorption studies would be performed if necessary in an attempt to explain any observed peculiarities in the mobility behaviour.

EXPERIMENTAL

Apparatus

Microelectrophoresis apparatus of the type described by Alexander and Saggers (1948) was used to measure the electrophoretic mobility. Conductance measurements were performed with a transformer type conductance bridge (Wayne Kerr Model B221) and a dip type conductivity measuring cell (Philips Model PW9510). pH measurements were made with a direct reading pH meter (E.I.L. Model 23A) using a calomel electrode–glass electrode assembly. Viscometry measurements over a variable range of shear were performed with a Couette viscometer, whose features have been described elsewhere (Hunter and Nicol, 1968).

Materials

The lithium and butylammonium vermiculites were samples kindly supplied by Dr. G. F. Walker of the Chemical Research Laboratories, C.S.I.R.O., Melbourne, and were similar to the material used in the swelling measurements.

Saturation of the clay with the respective counter-ions had been achieved by treatment with either lithium or butylammonium chloride (1 M) at 80°C until no further change in basal spacing could be detected by X-ray diffraction. Washing and centrifugal sedimentation of the clays yielded the following ranges of radii for the equivalent settling spheres: $0{\cdot}3\,\mu < r < 0{\cdot}8\,\mu$ (for Li) and $r < 0{\cdot}8\,\mu$ (for butylammonium). Butylammonium chloride was prepared by passing dry hydrogen chloride through a concentrated solution of butylamine in ether. The resultant precipitate of butylammonium chloride was recrystallised twice from dry acetone.

A modified (Friend, 1969) argentometric titration of chloride with dichlorofluoroscein as adsorption indicator showed the prepared butylammonium chloride to be quite pure to within the accuracy of the technique (i.e., ~ 0·2 per cent). The lithium chloride was of analytical reagent grade and all measurements were made at 20°C.

Methods

(i) *Determination of* ζ. ζ-potentials were calculated from the measured electrophoretic mobilities by applying the Smoluchowski equation (Overbeek, 1950) (1) in the region where it is applicable ($\kappa a > 100$):

$$U = \frac{\epsilon\zeta}{4\pi\eta} \tag{1}$$

where κ is the Debye–Hückel parameter (Verwey and Overbeek, 1948), a is the particle radius, U is the electrophoretic mobility, ϵ is the dielectric constant and η is the viscosity. For smaller values of κa the complete Booth expression (Booth, 1950) as presented by Hunter (1962), was used to take account of the relaxation and retardation effects.

(ii) *Adsorption studies and comparison of them with the mobility studies.* These were performed conductimetrically. The technique adopted was to equilibrate a concentrated (3–4 per cent) suspension of the clay in lithium chloride solution, the volume fraction of the clay being accurately known. Following centrifugation, the supernatant concentration of LiCl was compared with that calculated on the basis of the LiCl concentration being equal to the bulk value right up to the clay surface. The LiCl concentration of the supernatant was estimated by means of a calibration curve of conductance against concentration.

For quantitative comparison of the mobility and adsorption results it is possible to calculate from each of them the amount of negative adsorption, defined (van den Hul and Lyklema, 1967) for a particular ion i by

$$\Gamma_i = \int_0^\infty (C_i - C_i(x))\,\mathrm{d}x \tag{2}$$

where C_i is the actual bulk concentration and $C_i(x)$ is its value at a position x somewhere between the surface ($x = 0$) and the point where it becomes equal to C_i. The notation in this section is that of van den Hul and Lyklema (1967) as illustrated in Fig. 2, for a negatively charged surface. For material balance in the suspension

$$S\Gamma_i = V_t \Delta C_i \tag{3}$$

where S is the clay surface area, V_t is the volume of liquid and $\Delta C_i = C_i - C_o$ where C_o is the equilibrium electrolyte concentration for an uncharged surface.

$$\therefore\ \Gamma_i = \frac{V_t \Delta C_i}{S} \tag{3a}$$

For a specified system V_t is known, ΔC_i is measurable but to determine Γ_i the value of S must be known. The same adsorption measurements can also provide a value for S from the expression (van den Hul and Lyklema, 1967):

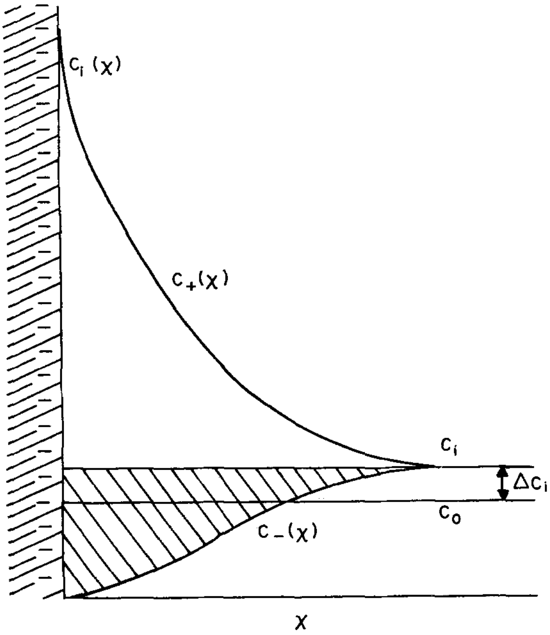

Fig. 2. Equilibrium distribution of ions at an uncharged surface (C_0) and a negatively charged surface (C_i) assuming the surface potential is $-\infty$ (from van den Hul and Lyklema, 1967).

$$S = \Delta V \cdot \frac{\kappa}{A'} \qquad (4)$$

where $\Delta V = V_t \cdot \Delta C_i / C_i$ and A' is a constant whose value, calculable from double layer theory is 2 for a symmetrical electrolyte.

An alternative expression for the negative adsorption of ions from the double layer is (Grahame, 1947):

$$\Gamma_i = A\left(\exp\left(\frac{ze\psi d}{2kT}\right) - 1\right) \qquad (5)$$

where $A = 17{,}580\ \sqrt{C_i}$ esu/cm^2. A slight underestimate of this may be involved in replacing ψ_d, the diffuse layer potential by ζ to determine Γ_i from the mobility measurements if the plane of shear does not correspond exactly with the Outer Helmholtz Plane (Grahame, 1947). Subject to this approximation equation (5) enables one to calculate negative adsorption from mobility measurements for comparison with the values obtained from equation (3a).

RESULTS

(a) Mobility measurements

The variation of zeta potential with counterion concentration is shown in Fig. 3. The behaviour is highly unusual and so considerable trouble was taken to ensure that no error or artefact was involved. Each mobility was the mean of two hundred readings achieving a standard deviation of 2 per cent. In addition, for points in the regions where unexpectedly large variations in the rate of change of mobility with concentration occurred, the whole procedure of suspension preparation and mobility measurement was repeated. In every case agreement to within the stated standard deviation was achieved. As stated above the Smoluchowski relation was used to convert the measured electrophoretic mobilities to zeta potentials. More reliable values of ζ are afforded by the method of Hunter (1962) which gives results corresponding closely to those calculated using the computer solution of Wiersema, Loeb and Overbeek (1966) and these are also shown in Fig. 4 for lithium; ζ is considerably increased in all cases but qualitatively the behaviour is the same. The latter is the important conclusion as the uncertainty in the value of 'a' for flat plates such as these must prevent unequivocal assessment of absolute ζ's irrespective of what method is used to convert U to ζ.

The behaviour of the double layer charge σ_2' is perhaps easier to interpret. It has been calculated on the basis of the simple Gouy–Chapman theory:

$$\sigma_2 = \sqrt{\frac{2\epsilon kTn}{\pi}}\sinh\left(\frac{ze\zeta}{2kT}\right) \qquad \text{(6) (Verwey and Overbeek, 1948)}$$

when n is the ionic concentration per cm^3, and other symbols have their usual meaning; a plot of σ_2 against concentration is shown in Fig. 5. Again peculiarities arise, the important feature being that over a narrow concentration range a sharp increase in diffuse layer charge (as expected with increase in concentration) rapidly changes into a sharp

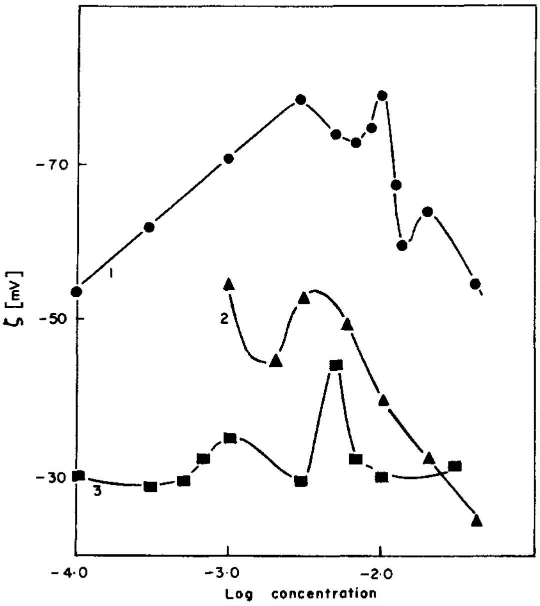

Fig. 3. Zeta potential as a function of bulk electrolyte concentration 1. Li vermiculite; 2. BuNH$_3$ vermiculite; 3. Na bentonite (Low, 1958).

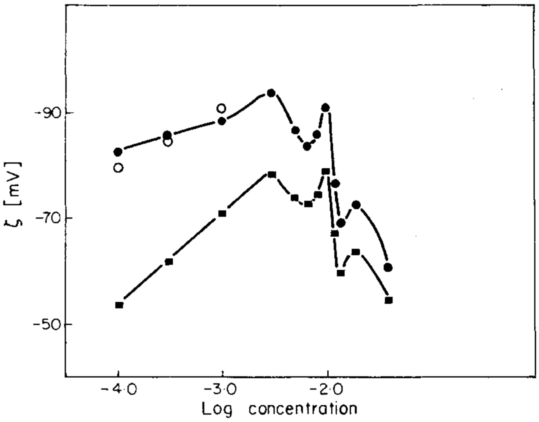

Fig. 4. Corrected zeta potential of Li vermiculite as a function of electrolyte concentration.
● Hunter's equation
○ Complete solution
■ Smoluchowski equation.

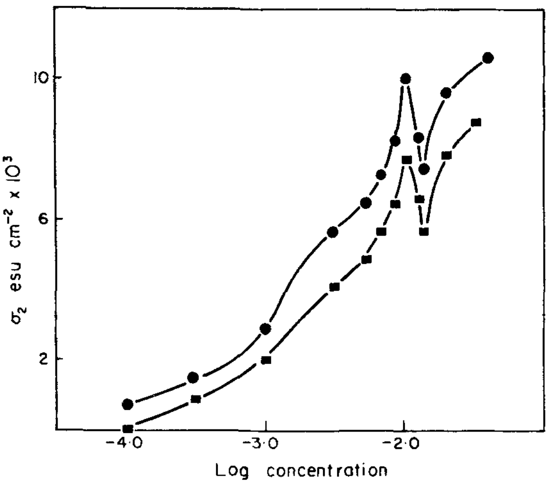

Fig. 5. Diffuse layer charge (σ_2) as a function of electrolyte concentration.

- ● calculated from Stigter and Mysels correction applied to ζ calculated from Hunter's expression
- ■ calculated from uncorrected ζ values.

decrease before once again rapidly resuming its increase.

(b) *Adsorption Measurements*

In an attempt to perhaps invoke some mechanism to explain the above results, a series of adsorption measurements for Li vermiculite in LiCl solution was performed. The procedure is described above, and the results of one of a series of measurements is shown in Fig. 6. The data is presented as a plot of $(C_i - C_0)/C_0$ against log C_i. Once again the behaviour is highly unusual with a large change in adsorption in the region of $1{\cdot}3 \times 10^{-2}$ M bulk LiCl concentration. A series of measurements at increasing and then decreasing concentrations showed the adsorption process to be reversible. The fact that C_i is generally larger than C_o is a commonly observed phenomenon known as negative adsorption. It is due to the expulsion of co-ions from the double layer by the charged surface. The results now plotted as A'/κ against ΔV are shown in Fig. 7. Because of the rather strange adsorption behaviour observed, the slope of the line of best fit must be considered to have a rather large uncertainty.

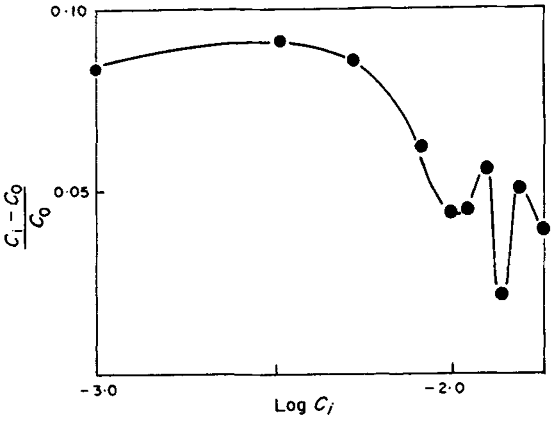

Fig. 6. Negative adsorption measurements as a function of bulk electrolyte concentration.

From this slope the surface area of the studied material was found to be 320 m^2/g.

Having determined S, equation (3a) was applied to determine Γ_i, which was then plotted against $\log_{10}C_i$ (Fig. 8). Variations in the negative adsorption as a function of electrolyte concentration, similar to those observed in the ζ potential measure-

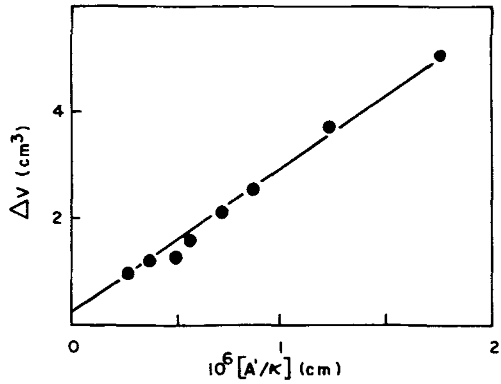

Fig. 7. Determination of surface area by the method of van den Hul and Lyklema (1967).

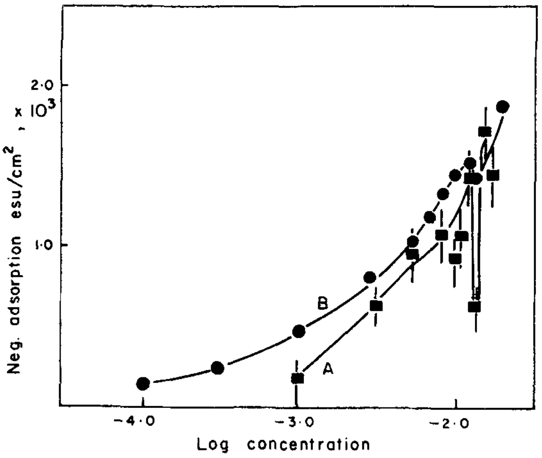

Fig.8. Comparison of negative adsorption calculated from (A) the adsorption results and (B) the mobility results.

ments above were apparent and these two independently derived series of Γ_i values are compared in Fig. 8. It can be seen that there is quite good correspondence between the two curves, there being a distinct minimum at exactly the same concentration in each case. There appeared to be poor agreement between the actual depths of these minima, no doubt related to the fact that in the adsorption case the depth of the negative adsorption minimum was not reproducible.

(c) *Rheological measurements*

The values of Γ_i obtained from adsorption data at higher ionic strength are seen to be considerably lower than the corresponding values of Γ_i from mobility data.

If any premature flocculation or association of the sol occurred at the higher ionic strengths it would be expected that lower values of Γ_i (determined from the adsorption data) would be obtained. The rheological behaviour of the above suspensions was therefore, determined and compared with that of a visibly flocculated suspension (volume fraction of clay being constant). The respective shear diagrams (Fig. 9) for the suspensions under examination were identical to a high degree of accuracy. There appears to be no trend towards the non-Newtonian characteristics shown by the flocculated suspension. The distinguishing features of the latter are a viscosity varying with shear rate and a non zero shear stress at zero shear rate.

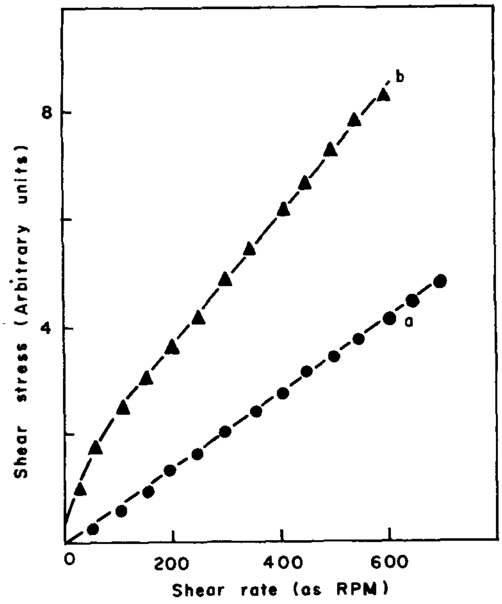

Fig. 9. Shear behaviour of the examined suspensions compared with that of a flocculated suspension. (a) represents three different electrolyte concentrations (1·0, 1·35 and 3·13 × 10^{-2}M) covering the range of interest and (b) represents a suspension at the same volume fraction of clay (0·023) which had been visibly flocculated by the addition of sodium chloride.

DISCUSSION

(i) *Correlation with earlier results*

The above highly unusual zeta potential and charge behaviour is not unique as some time ago Low (1958), working with sodium bentonite, observed similar microelectrophoretic behaviour. His results are plotted with ours in Fig. 3. He was also able to relate the unusual variation of ζ to almost exactly the same variation in another independently measurable quantity. This was the clay concentration to which a concentrated suspension at a particular electrolyte concentration had to be diluted to cause freezing at a specific temperature. More recently Davidtz (1968) has shown without comment an abrupt change in the modal temperature of spontaneous freezing of clay suspension (montmorillonite in NaCl solution) droplets in oil at approx. 10^{-2} M NaCl. Another interesting correlation comes from analysis of the original swelling measurements. For example, closer examination of the variation of interlayer distance with electrolyte concentration for the swelling of butylammonium vermiculite shows that the linear relationship assumed by Garrett and Walker (1962) is in fact a considerable approximation. Their results (Fig. 10) show an abrupt change in plate separation in the same region as our microelectrophoresis and adsorption results. Therefore in some respects there appears to be a parallel between our results and the swelling results.

For a more quantitative comparison, however, we have calculated, form the measured mobilities, theoretical equilibrium spacings using the D.L.V.O.

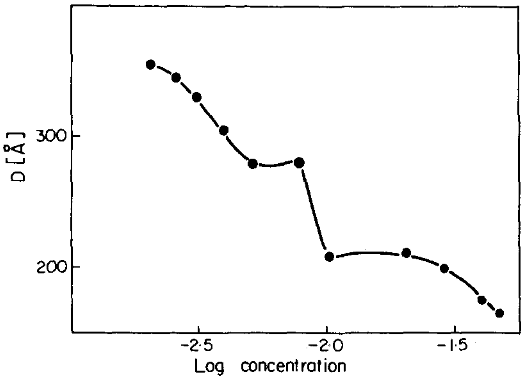

Fig. 10. Interlayer distance of butylammonium vermiculite as a function of butylammonium chloride concentration (reinterpretation of the results of Garrett and Walker, (1962).

theory. In all cases the calculated spacings were far in excess of the measured ones. For example at 10^{-3} M, the measured spacing was smaller than the predicted one by a factor of 4–5. As the theoretical repulsive force between clay plates has been quite convincingly confirmed (see Introduction) it would appear that this smaller than predicted swelling may be caused by an additional attractive force. Although vermiculite was originally chosen to avoid the problem of edge-to-face interaction, which is known to occur in montmorillonite, there is a slight possibility that such a phenomenon occurs here. A model of intercalation of some plates at various angles between the generally parallel plates would predict that at plate separations too small for intercalation of plates the theoretical spacing would be observed. This appeared to be the case, for in assuming the Hamaker constant A to be 2×10^{-12} ergs, for 10^{-3} M electrolyte, the theoretical and measured values of the half distance of separation d were 910 and 170 Å respectively, and for 4×10^{-2}M, they were 62 and 65 Å respectively.

(ii) *Surface area determination*

As reported above the surface area of 320 m^2/g determined by negative adsorption for lithium vermiculite is about half that expected on the basis of the crystal geometry. However, this assumes swelling, i.e. complete separation, of all clay plates, an assumption which has been increasingly questioned. Unequivocal evidence supporting the idea that plate separation is not complete has come recently from the work of Barclay and Thompson (1969). They have produced electron micrographs of the edges of swollen sodium montmorillonite crystals showing approximately three unexpanded primary plates per swelling unit. In our case an average of two unexpanded plates per swelling unit would explain the low surface area.

(iii) *The anomalous behaviour at about 10^{-2}M electrolyte concentration*

The swelling measurements of Garrett and Walker (1962) show that over a narrow concentration range in the region of 10^{-2}M, the average interlayer spacing changes sharply from 280 Å to 210 Å. If we assume that particles are collapsing two at a time it can be shown that *ca.* 45 per cent of the constituent plates must collapse to cause this change in the average interlayer spacing (the latter was determined from the macroscopic swelling of a large crystal). If this happened it would account for a 25 per cent decrease in surface area from the expected value. Any such aggregation at a particular concentration, effecting the surface area, will cause an error in the negative adsorption as calculated by the method of van den Hul and Lyklema (1967). It can be seen that consideration of such an effect increases the calculated negative adsorption (since $\Gamma_i \propto 1/S$) and so reduces the discrepancy in Γ_i, as calculated by the two methods, in the region where the sharp minimum in Γ_i occurs. It is, however, rather difficult to reconcile this with the rheological data since any such collapse, if it were reversible, should give rise to an increase in apparent viscosity (Hunter and Nicol, 1968) and no viscosity anomaly was observed in this concentration region.

We must now examine in more detail the variation of ζ and diffuse layer charge (σ_2) with electrolyte concentration and, in particular, the very sharp fall at *ca.* 10^{-2}M, far in excess of anything expected simply on the basis of double layer contraction with increasing ionic strength. The adsorption results indicate that some significant adsorption change is occurring in this region.

In an attempt to throw some light on the above phenomena several possible processes at the clay water interface can be considered.

(a) *Effect of the oxide surface*

Considerable evidence (Anderson and Low, 1958; Low, 1961; Deryaguin and Greene-Kelly, 1964; Deryaguin, 1966; Davidtz, 1968) has been accumulated supporting the contention that an oxide surface can structurally influence water adjacent to it. Whether this occurs in the lithium vermiculite case, however, has recently been cast in doubt by some neutron scattering measurements (Hunter, Stirling and White, 1969). These appear to indicate that no more than one water layer is bound to the surface, water layers further out appearing to have bulk mobility. It would seem doubtful therefore, that the concept of water structuring further out than one or two water molecule diameters from the surface, can be used.

(b) *Effect of electrolyte*

Vaslow (1966) and Good (1964) have shown that there are significant changes in structure-related properties of water at high concentrations of LiCl. At about 1M, Vaslow found a sharp discontinuity in the rate of change of the apparent molal volume, while Good found that the energy of activation for fluid flow was a maximum at *ca.* 0·5M. The question is: "Can possible structural changes in LiCl solutions at this order of concentration be related to the unusual behaviour of vermiculite in much more dilute solutions ($\leqslant 4 \times 10^{-2}$)?". When one considers the effective concentration in the neighbourhood of a highly charged surface, this may be a real possibility. We can examine its significance using the Stern

(Verwey and Overbeek, 1948) picture of the double layer and the following assumptions: values for σ_1, the Stern layer charge density are evaluated as volume concentrations of Li^+; taking the hydrated radius of Li^+ as 3·74 Å (Robinson and Stokes, 1965), and of water as 1·4 Å, and using the picture of Bockris, Devanathan and Müller (1963) for the inner part of the double layer we find that σ_1 varies from 2·0 to 1·7 M as the bulk electrolyte concentration ranges from 10^{-4} to 4×10^{-2} M. Slightly further out from the surface the concentration of Li^+ would be in the 0·5–1 M region where the bulk results (Vaslow, 1966 and Good, 1964) indicate significant aqueous structural changes. It seems, therefore, that, at least in the case of lithium vermiculite, the effect of the counter ion near the surface on the water structure may be of relevance in explaining a sharp change in the observed parameters.

CONCLUSION

It appears that although the lithium vermiculite system has at first sight the necessary characteristics to permit a definitive test of the double layer interaction theory for infinite flat plates, there are some considerable difficulties associated with this system. Some rather characteristic effects apparently occur at a concentration around 10^{-2}M and these have a profound influence on the aggregation of the particles. The precise nature of these effects remain obscure but they appear to be associated with some structural changes in the electrolyte near the clay surface, and are reflected in changes in adsorption, aggregation and other surface influenced phenomena. It would therefore seem that the swelling clay systems can only assume a rather limited role in the testing of double layer theories for flat plates.

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Résumé — Le comportement microélectrophorétique et d'absorption de la vermiculite de lithium a été étudié en tant que fonction de la concentration du chlorure de lithium. Ceci a été effectué au cours d'une tentative visant à établir l'applicabilité de tels systèmes à l'essai des théories d'interaction de plaques planes et, se faisant, de jeter une plus grande lumière sur les mesures de gonflement effectuées sur ces matériaux. Le comportement étudié, bien que très inhabituel, donnait un accord assez satisfaisant entre les paramètres microélectrophorétique et d'absorption et s'accordait, qualitativement, avec certaines mesures antérieures sur des matériaux similaires.

Les propriétés observées semblent être dues à certains effets spécifiques de structure, soit de la surface oxyde ou des ions de l'électrolyte. Si cela est, ces systèmes sont loin d'être des modèles idéaux pour l'essai de la théorie d'interaction de deux plaques planes uniformes.

Kurzreferat — Das mikroelektrophoretische und Adsorptionsverhalten von Lithiumvermiculit in Abhängigkeit von der Lithiumchloridkonzentration wurde untersucht. Das geschah im Rahmen eines Versuches die Anwendbarkeit solcher Systeme auf did Prüfung von Theorien über die gegenseitige Wirkung flacher Platten festzustellen, und auf diese Weise mehr Licht auf die an solchen Stoffen ausgeführten Messungen der Aufquellung zu werfen. Das untersuchte Verhalten war wohl ungewöhnlich, zeigte jedoch gute Übereinstimmung zwischen Adsorptions- und mikroelektrophoretischen Parametern und stimmte, qualitativ, mit früheren Messungen an ähnlichen Stoffen überein.

Die beobachteten Eigenschaften scheinen die Folge gewisser struktureller Wirkungen entweder der Oxydoberfläche oder des Elektrolytions zu sein. Sollte das der Fall sein, so sind diese Systeme alles eher als ideale Modelle für die Prüfung der Theorie über die gegenseitige Wirkung zweier gleichförmiger flacher Platten.

Резюме—Проведено изучение микроэлектрофоретических и адсорбционных свойств литиевого вермикулита в зависимости от концентрации хлорида лития. Исследование предпринято с целью выяснения возможности использования таких систем для проверки теории взаимодействия плоских пластин и для более правильного истолкования набухания подобных материалов. Изученные свойства хотя и являются весьма необычными, но все же позволяют говорить о хорошем соответствии адсорбционных и микроэлектрофоретических параметров; качественно они согласуются с результатами некоторых ранних исследований аналогичных материалов.

Изученные свойства, по-видимому, обусловлены в первую очередь специфическими структурными эффектами, свойственными как окисным поверхностям, так и электролитическим ионам. Если это действителъно так, то подобные системы являются далеко не идеальными моделями для проверки теории взаимодействия двух одинаковых плоских пластин.