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SWELLING OF n-BUTYLAMMONIUM VERMICULITE IN WATER

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Abstract—The swelling of an n-butylammonium vermiculite in solutions of n-butylammonium chloride has been studied by neutron diffraction as a function of temperature and the concentration of the soaking solution. On heating a swollen sample a transition to the crystalline phase took place at a well-defined temperature, the *c*-axis spacing changing from 120 to 19.4 Å at 14°C in a 0.1 M solution and from 330 to 19.4 Å at 33°C in a 0.01 M solution. The phase transition was completely reversible, and a study of the temperature-concentration phase diagram was made as high as 50°C. The swollen phase was studied in a range of concentrations of the external solution between 0.2 M and 5×10^{-4} M, for which the *c*-axis spacings were 85 and 910 Å, respectively. The reversibility, sharpness, and reproducibility of the phase change from crystalline to swollen gel suggest that the transition is truly thermodynamic, which is not in accord with DLVO theory. The concentration dependence of the observed d-values also could not be explained satisfactorily by DLVO theory.

Key Words—DLVO theory, n-Butylammonium chloride, Neutron diffraction, Swelling, Vermiculite.

INTRODUCTION

The swelling of vermiculite in water is an unusual phenomenon. Some single crystals swell anisotropically perpendicular to the plane of the silicate layers, leading to increases in volume of as much as 4000%. The resulting water spacings are sufficiently large that the system behaves as a one-dimensional colloid. This phenomenon was first reported by Walker (1960) and investigated for a variety of vermiculite samples by Garrett and Walker (1962). They found the expansion to be most uniform for a Kenya vermiculite, which had a layer charge of 1.3 univalent cations per $O_{20}(OH)_4$ structural unit. They also commented that for some alkylammonium vermiculite samples the swelling was dependent on temperature. The expansion of vermiculite as a function of swelling pressure was also studied by Rausel-Colom (1964) and Norrish and Rausel-Colom (1963) and more recently by Viani *et al.* (1983, 1985).

The present report concerns a different vermiculite treated over a much wider range of conditions. In particular, neutron diffraction was used to determine the equilibrium swelling to much larger d-values than previously. The temperature dependence of this equilibrium was also monitored.

EXPERIMENTAL

Crystals about 50 mm^2 in area by 1 mm thick were cut or cleaved from larger blocks of Eucatex vermiculite (from Eucatex, Brazil). Homoionic forms were prepared using the procedure of Garrett and Walker (1962). The crystals were washed and then treated for about six months with 1 M NaCl solution at 50°C, with regular changes of solution, to produce a pure sodium vermiculite. The completeness of the exchange was checked from the regularity of the *c*-axis peaks in the X-ray and neutron diffraction patterns, the *c*-axis spacing for the sodium form being 14.9 Å. To prepare the n-butylammonium vermiculite the sodium form was soaked in 1 M n-butylammonium chloride solution at 50°C, with regular changes of solution, for two weeks. The purity was again checked by X-ray and neutron diffraction, the *c*-axis spacing now being 19.4 Å. In approximate agreement with Garrett and Walker, the crystals did not swell if the concentration of electrolyte exceeded about 0.4 M. The crystals were therefore stored in 1 M solution.

Most of the diffraction experiments were carried out on the D16 long-wavelength neutron diffractometer at the Institut Laue-Langevin. The incident wavelength was 4.52 Å with a wavelength spread $\Delta\lambda/\lambda$ of about 2%, which is suitable for studying *c*-axis spacings in the range 2–350 Å. For larger spacings, the D17 and D11 small-angle diffractometers at Institut Laue-Langevin were used. Spacings to about 650 Å were measured on the D17 diffractometer, which used incident wavelengths in the range 10–30 Å. The D11 instrument offers wavelengths between 2 and 20 Å and is equipped with a multidetector and collimators, which can be positioned at distances of 2, 5, 20, and 40 m from the sample, allowing measurements of *c*-axis spacings as great as 2000 Å. A fuller description of the three instruments used is given in Institut Laue Langevin (1986).

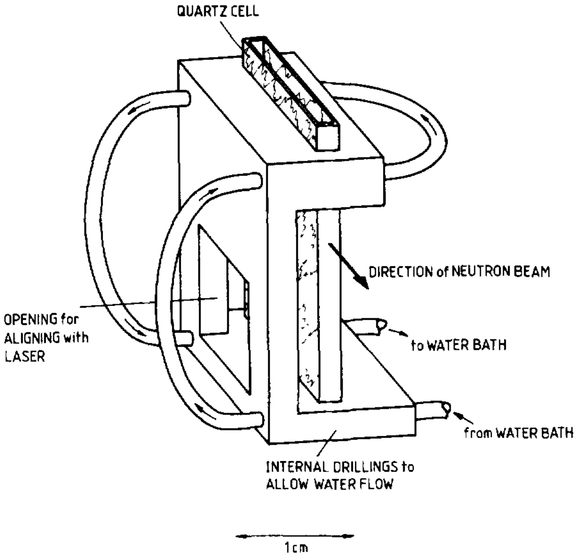

Figure 1. Arrangement for heating the quartz sample cell.

The samples for the diffraction experiments were prepared as follows. A crystal of the n-butylammonium vermiculite was cut to a thickness of about 0.5 mm and an area of about 5 × 5 mm^2 and soaked in the appropriate solution of protonated n-butylammonium chloride in D_2O. D_2O was used because it gave a lower incoherent scattering background than H_2O. The crystal was allowed to come to its equilibrium swelling distance for 24 hr at a temperature of 7°C. The macroscopic expansion was measured by means of a traveling microscope. A slice of this swollen crystal about 1 mm thick was then transferred to a quartz cell of internal dimensions 30 × 5 × 2 mm. The remainder of the quartz cell was filled with some of the original solution. The cell was sealed with parafilm to prevent loss of solution by evaporation, clamped into an aluminum block as shown in Figure 1, and allowed to equilibrate at the required temperature. The temperature of the block was controlled by circulating water from a bath whose temperature was maintained at ±0.2°C. The aluminum block was mounted on a standard goniometer, and the crystal was aligned accurately in the neutron beam by means of a laser.

RESULTS

Crystalline phases

The swelling of clays is conveniently divided into two regions, the first of which corresponds to the uptake of a relatively small proportion of water, possibly as much as about 4 molecular layers; the second region involves the uptake of much larger volumes of water. The two types of swelling are distinct and are often referred to as interlayer or crystalline swelling and "osmotic" swelling, respectively (van Olphen, 1977). The same pair of terms is used here.

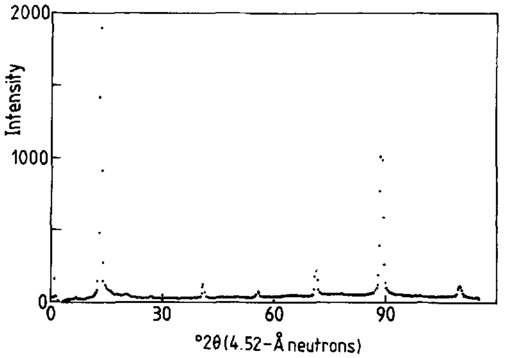

Figure 2. Neutron diffraction pattern of fully hydrated crystalline phase of n-butylammonium vermiculite measured in reflection geometry. $\lambda = 4.52$ Å.

At relative humidities (RH) somewhat less than 100% n-butylammonium vermiculite exists in two stable crystalline phases having *c*-axis spacings of about 15 and 19 Å and a number of poorly characterized, metastable intermediate phases (Humes, 1985). The metastable intermediate phases correspond to different states of hydration of the counterion or of the surface of the clay platelet, and changes between them are brought about by changes in RH. For a sample soaking in 1 M n-butylammonium chloride the equilibrium structure should be a 19.4-Å phase, for which the first order *c*-axis peak is at about 14°2θ for an incident wavelength of 4.52 Å.

The diffraction pattern of this phase is shown in Figure 2. The range of the instrument was sufficient to show the first seven orders of the $00l$ reflection. Only this series of peaks was observed, because the experiment was done in reflection with the momentum transfer perpendicular to the plane of the crystal, and because the mosaic spread of the crystal was small. For the sample whose pattern is shown in Figure 2 the mosaic spread was determined by a rocking curve. The rocking curve was measured by rotating the sample about its vertical axis (angle ω), while 2θ was fixed at the peak of the 001 reflection. The angular width of a rocking curve, ω, is an accurate measure of the spread in orientation of the crystallites making up a crystal. Here, the full width at half height of the rocking curve, shown in Figure 3, was found to be 5.3°ω. This value is therefore the mean spread in orientation of the platelets in the crystalline vermiculite and was typical of all the crystals examined. Some $\lambda/2$ contamination of the pattern is apparent in Figure 2, and a broad maximum in the background is present, peaking near the 005 reflection. The maximum is probably a very weak contribution from the quartz cell and solution.

The intensities of the peaks in Figure 2 contain information about the distribution of scattering intensity within the unit cell. More complete measurements on samples of different isotopic composition were also made over a more extensive region of reciprocal space

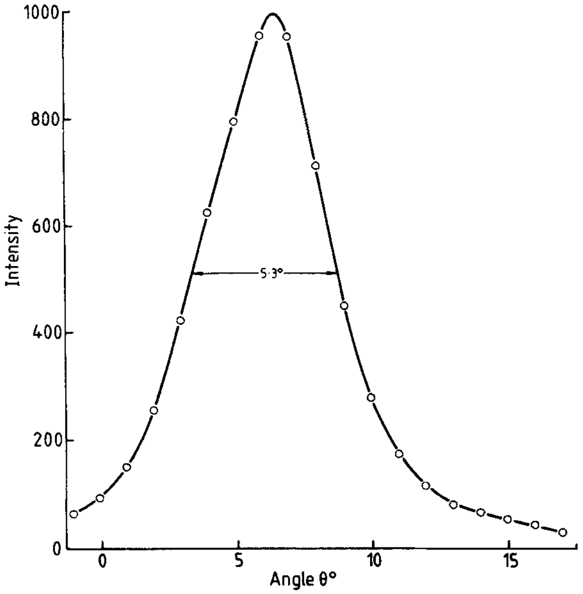

Figure 3. Rocking pattern on 001 peak of crystal of fully hydrated n-butylammonium vermiculite.

using the D19 diffractometer at the Institut Laue-Langevin and will be used for a full structure determination of the 19.4-Å phase, to be reported elsewhere. In the present report, the pattern has only been used to verify the purity of the crystal and as a "fingerprint" to identify the crystalline phase. For completeness, however, the relative intensities of the 00*l* reflections are listed in Table 1.

Swollen phase

An "osmotically" swollen phase was studied in a range of concentrations of the external n-butylammonium chloride solution between 0.2 M and 5 × 10^{-4} M. Macroscopic swellings as measured by a traveling microscope for concentrations of 10^{-1}, 10^{-2}, and 10^{-3} M were found to be about 6-, 16-, and 32-fold, respectively. Macroscopic measurements of more dilute gels were difficult owing to their fragility and transparency. On swelling the vermiculite, the diffraction patterns changed completely, the peaks associated with the crystalline phase disappearing and new, broader peaks appearing at low angles. The pattern of the 0.1 M sample at 6.2°C (Figure 4) shows an intense first-order peak having a spacing of 122 Å, a weak second-order peak, and a third-order peak. The third-order peak is not clearly evident on the scale of Figure 4, but was seen on an expanded scale. The pattern is shown with a 2θ scale to 20° to demonstrate the absence of the very intense first-order peak of the crystalline phase. The scale of Figure 4 is considerably expanded compared with that of Figure 2, the low-angle pattern being much weaker than the high-angle pattern.

Table 1. Relative intensities of 00*l* reflections of the fully hydrated crystalline phase.

Order	°2θ[1]	d-value (Å)	Intensity
—	6.60	—	27(λ/2)
1	13.38	19.44	4909
2	27.02	19.40	49
3	41.03	19.38	265
4	55.80	19.36	105
—	63.82	—	15(λ/2)
5	71.67	19.35	511
6	89.11	19.38	4295
7	110.02	19.32	389

Intensity is given in arbitrary units. Two weak peaks in the pattern arise from order contamination (λ/2).

[1] CuKα radiation.

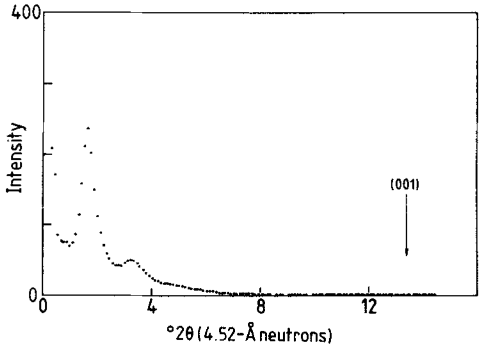

Figure 4. Low-angle diffraction pattern of n-butylammonium vermiculite at 6.2°C and an external concentration of 0.1 M.

The microscopic expansion from 19.4 to 122 Å matches the six-fold macroscopic expansion almost exactly, confirming the assertions of other authors (Walker, 1960; Garrett and Walker, 1962; Rausel-Colom, 1964; Norrish and Rausel-Colom, 1963; Viani *et al.*, 1983, 1985) that expansion in this material was perfectly homogeneous. What is perhaps more remarkable is that the orientation of the platelets was largely retained in the expansion, as demonstrated by the rocking curve on the first-order peak of the low-angle pattern, shown in Figure 5. The full width at half height was 6.5°ω, scarcely different from that for the crystalline material.

Dependence of osmotic swelling on temperature

Heating the osmotically swollen samples at a well-defined temperature brought about a transition to the crystalline phase. For example, for the sample at an external solution concentration of 0.1 M, no change was detected in the diffraction pattern on heating to 13.5°C, but at 14.5°C the low-angle pattern shown in Figure 4 had collapsed into a broad envelope of scattering, and the pattern of the crystalline phase reappeared. Further scans at 20°, 25°, and 30°C were identical to that at 14.5°C, showing that the phase change was complete in the interval 13.5°–14.5°C. The tran-

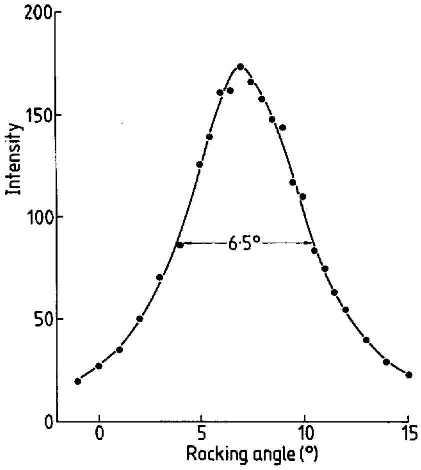

Figure 5. Rocking pattern on the 001 peak of the swollen phase of n-butylammonium vermiculite at 6.2°C and an external concentration of 0.1 M. d-value = 122 Å.

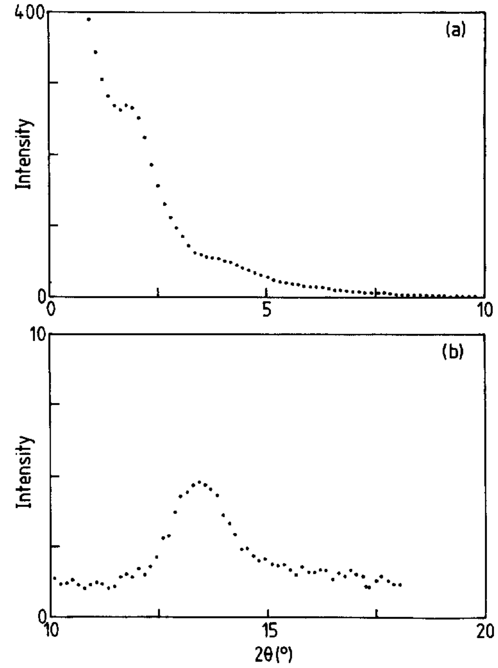

Figure 6. Neutron diffraction pattern of n-butylammonium vermiculite close to the crystalline-swollen phase transition at 14.1°C and a concentration of external solution of 0.1 M. (a) low-angle region; (b) wide-angle region.

sition was shown to be reversible by cycling the temperature between 10° and 20°C. The *c*-axis spacing was always found to be in the range 120–125 Å at <13.5°C, and the full diffraction pattern of the crystal was always recovered at >14.5°C.

At temperatures close to the phase transition some variation of the *c*-axis spacing was found. Figure 6 shows the pattern obtained at 14.1°C. The low-angle diffraction pattern (Figure 6a) corresponds to a spacing of 140 Å, and the presence of a crystalline phase is shown by the presence of the first-order peak (Figure 6b). The intensity of this peak, however, was about one quarter of the value observed at higher temperatures. Close to the center of the temperature range of the phase transition (14°C), the vermiculite took on a silvery sheen. The sheen always appeared at the phase transition and could therefore be a possible means of following the phase transition experimentally.

At an external concentration of 10^{-2} M the macroscopic swelling indicated a *c*-axis spacing of about 330 Å. The low-angle diffraction pattern obtained on the D17 instrument using an incident wavelength of 17 Å (Figure 7) had first- and second-order peaks also corresponding to a spacing of 330 Å. This spacing was also measured on the D16 instrument. Some arguments have existed about the possible contribution of specular reflection from either the clay or the cell to these diffraction patterns (Brindley and Simonton, 1984; van der Gaast and Jansen, 1985; Simonton, 1984). At these low angles specular reflection may be confused with diffraction peaks; however, we were able to use the mosaic spread of the crystals to rotate the sample until contributions from specular reflection, which were indeed observed, vanished. Figure 7 corresponds to just such an orientation. The neutron experiment, under these conditions, had much higher resolution than a laboratory-based X-ray diffraction instrument, and no difficulties were encountered due to experimental artefacts in this range of d-values.

For the sample at 0.01 M, the temperature was changed in approximately 2° steps between 21.7° and 34.3°C (see Figure 8). The intensity of the first-order peak varied with temperature, reaching a minimum at about 27°C, but its position was unchanged to a temperature of 30.4°C. At 32.3°C it appeared at a slightly lower angle, just as was observed for the 0.1 M sample at 14°C, and at 34.3°C it was obliterated by a broad envelope of small-angle scattering. Parallel experiments on the D16 instrument showed that the pattern of the crystalline phase was just visible at 33.5°, but not at 32.6°C. At 35°C the sample was fully crystalline.

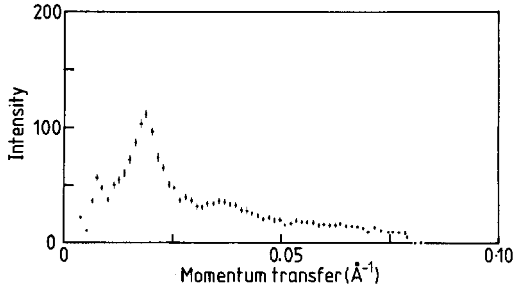

Figure 7. Low-angle diffraction pattern of swollen phase of n-butylammonium vermiculite at 21.7°C and a concentration of 10^{-2} M. λ = 17 Å.

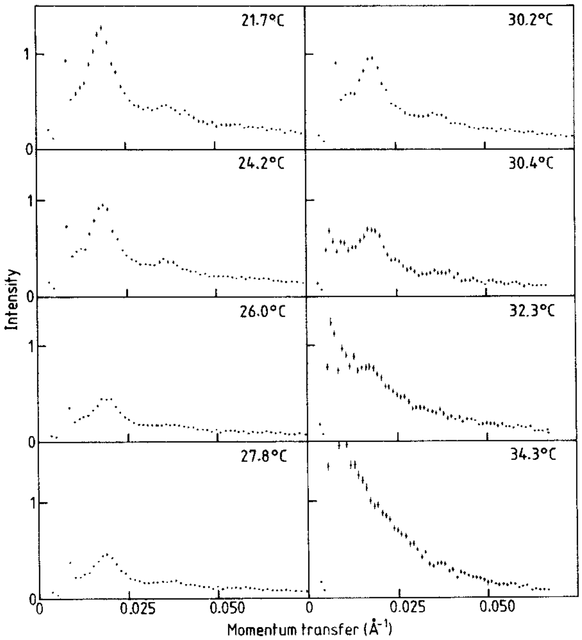

Figure 8. Temperature-induced phase transition between the swollen and crystalline phases of n-butylammonium vermiculite at an external concentration of 10^{-2} M. $\lambda = 17$ Å.

Thus, the phase transition at 0.01 M shifted from 14°C at 0.1 M to 33°C at 0.01 M.

Similar experiments at 10^{-3} M gave a *c*-axis spacing of 680 Å and a transition temperature of 45°C, verified also by both the change in the low-angle pattern and the appearance of the crystalline diffraction pattern using the D16 and D17 instruments. This *c*-axis spacing was also reproduced on the D11 instrument, which allowed spacings as large as 900 Å to be observed for a 5×10^{-4} M solution.

The experiments described above were all made on slices of vermiculite taken from one swollen crystal. Experiments on samples from different swollen crystals, all in 0.1 M solution, yielded d-values in the range 110–125 Å. Not all of this variation can necessarily be attributed to crystal variation, because some uncertainty existed in the final concentration of the n-butylammonium chloride solution in such small sample cells. The observed range of values, therefore, represents the maximum variability attributable to the vermiculite.

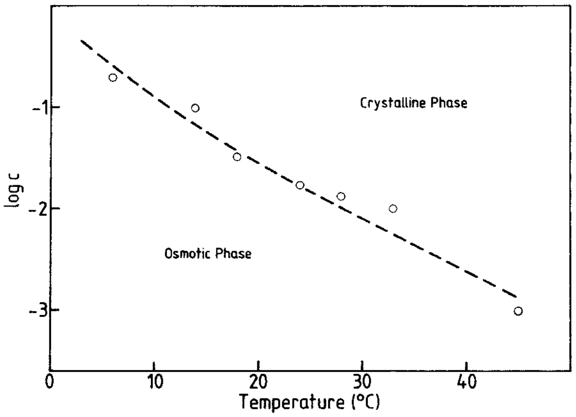

Figure 9. Temperature-concentration (c) phase diagram of n-butylammonium vermiculite.

Table 2. Swelling temperatures and spacings for n-butylammonium vermiculite.

Concentration (M)	*c*-axis spacing (Å)	Temperature (°C)
0.2	85	6
0.1	120	14
0.09	125	—
0.08	145	—
0.06	145	—
0.05	155	—
0.03	190	—
0.02	225	—
0.01	330	33
0.003	440	—
0.001	680	45
0.0005	910	—

Phase transition temperature was only determined for four of the concentrations in the table.

A summary of the swelling temperatures and d-values obtained for the various solution concentrations is given in Table 2, and the phase diagram for the transition is shown in Figure 9.

DISCUSSION

The reversibility, sharpness, and reproducibility of this unusual phase change from crystalline to osmotically swollen gel show that it must have been a true thermodynamic transition. In DLVO theory, all hydrophobic sols are thermodynamically unstable because the minimum in the potential energy of interaction at short distances is deeper than the weak secondary minimum at large distances, which arises from the interplay of electrostatic and van der Waals forces (Derjaguin *et al.,* 1987). A reversible transition between crystalline and swollen phases is therefore not possible within the framework of DLVO theory. The results apparently disagree qualitatively with the theory. An additional short-range repulsion, which modifies the relative depths of the two potential energy minima, would have to be introduced into the DLVO theory to account for the discrepancy.

At large distances the two long-range forces included in the DLVO theory will be dominant and, although the attractive van der Waals interaction cannot be calculated explicitly, the theory gives a quantitative prediction of the repulsive electrostatic interaction for the interaction of a pair of plates. It is instructive to compare the concentration dependence of the observed d-values (Table 2) with those predicted by the DLVO theory. Other authors have found large discrepancies

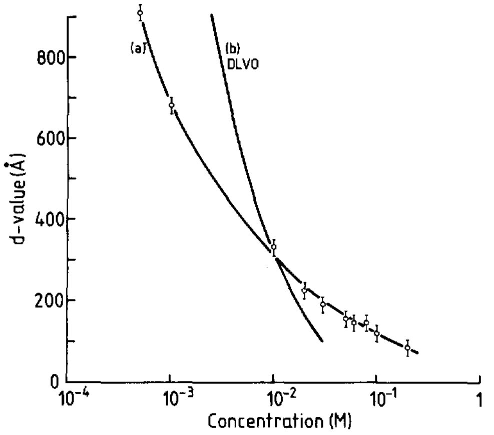

Figure 10. Comparison of experimentally observed (a) and calculated d-values using DLVO theory (b), with the single adjustable parameter (proportional to the Hamaker constant) chosen to fit the data at 10^{-2} M.

between predicted and observed values (see, e.g., Hunter, 1987; Viani *et al.*, 1983, 1985).

The DLVO model postulates that the appropriate thermodynamic potential energy of interaction between two parallel flat plates can be described in terms of two components: a repulsive term V_R, resulting from the overlap of electrical double layers; and an attractive van der Waals interaction, V_A. It also assumes that these interactions are additive, so that the total potential energy can be written as

$$V = V_R + V_A.$$

Both the Boer-Hamaker treatment (de Boer, 1936; Hamaker, 1937) and the macroscopic approach of Lifschitz (1955) yield an inverse cubic decay of the attactive van der Waals force,

$$\frac{dV_A}{dx} = A'/x^3.$$

for small separations x. At large separations, retardation reduces the attactive force, resulting in the equation

$$\frac{dV_A}{dx} = A/x^4.$$

The force of attraction between the two plates is now inversely proportional to the fourth power of the separation. Because the present investigation deals with separations between 100 and 1000 Å, the latter equation is applicable. A is considered to be an arbitrary constant, because it cannot be calculated *a priori.* The double layer repulsion, V_R, at large distances, is given by the equation

$$V_R \propto \frac{1}{\kappa} \exp(-\kappa x)$$

where κ is the inverse Debye screening length given by

$$\kappa^2 = \frac{2n_0q^2}{\epsilon kT},$$

where n_0 is the number density of ions, q is the charge of the ions, ϵ is the permittivity of the medium, k is the Boltzmann constant, and T the absolute temperature. For monovalent ions in aqueous solution at 25°C

$$\kappa^2 = 0.1c,$$

where κ has units of $Å^{-1}$ and c has units of mole/liter.

From the sharpness of the phase transition the observed d-values should clearly be treated as equilibrium separations of the platelets; thus the repulsive and attractive forces $\frac{dV_A}{dx}$ and $\frac{dV_R}{dx}$ must balance.

Because

$$\frac{dV_R}{dx} = B\exp(-\kappa x),$$

where B is a constant determined from electrostatic theory,

$$B\exp(-\kappa x_{eq.}) = A/x_{eq.}{}^4.$$

Denoting the equilibrium separation $x_{eq.}$ by d, and writing A/B = C,

$$d^4\exp(-\kappa d) = C.$$

Theory and experiment can now be compared by choosing C such that d = 320 Å for $\kappa = 0.0316$, i.e., for a concentration of 10^{-2} M, so that the results agree in the middle of the concentration range studied. This gives $C = 4.26 \times 10^5$ $Å^4$; the curve

$$d^4\exp(-\kappa d) = 4.26 \times 10^5\ Å^4$$

is plotted together with the experimental curve in Figure 10. This diagram shows that, in agreement with other authors, the DLVO theory does not account for the variation of d-values with concentration in this system.

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