EFFECT OF HYDROSTATIC PRESSURE ON THE SWELLING OF n-BUTYLAMMONIUM VERMICULITE

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Abstract—The osmotic swelling of an n-butylammonium vermiculite in a 0.1 M solution of n-butylammonium chloride has been studied as a function of temperature and hydrostatic pressure by neutron diffraction. On application of a pressure of 1050 bar the vermiculite swelled macroscopically at 20°C, the *c*-axis spacing changing from 19.4 to 126 Å. The phase transition was completely reversible with respect to both pressure and temperature, and a complete study of the temperature-pressure phase diagram was made at pressures as high as 2000 bar. The heat capacity change with temperature across the swelling transition was measured at atmospheric pressure, and the enthalpy and entropy of the change from crystalline to osmotic phases were found to be, respectively, 5.2 J/g and 0.0183 J/K·g of dry clay. The combination of the entropy change with the gradient of the pressure-temperature phase boundary gave the volume change accompanying the transition. The total volume of the swollen phase was less than that of the crystalline phase plus the appropriate amount of solution, corresponding to a fractional decrease of about 0.1% in the water volume from bulk solution to between the plates.

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

INTRODUCTION

The uniaxial swelling of n-butylammonium vermiculite crystals in dilute solutions of n-butylammonium chloride was first reported by Walker (1960), and the macroscopic characteristics of the process were described for a variety of different vermiculite samples by Garrett and Walker (1962). Early X-ray diffraction studies by Rausel-Colom (1964) and Norrish and Rausel-Colom (1963) indicated that the macroscopic expansion of these crystals exactly matched the microscopic *c*-axis expansion to the limit of experimental error for plate separations as large as about 200 Å, the original crystals having a *c*-axis spacing of 19–20 Å. Braganza *et al.* (1989) used neutron scattering to follow the swelling and obtained similar results for *c*-axis spacings of about 900 Å.

An unusual feature of the swelling of the vermiculite is that it is extremely sensitive to the temperature. This sensitivity is not predicted by simple DLVO theory and presumably has its origin in a strong temperature-dependent adsorption of the n-butylammonium ion on the clay. A factor which may affect the adsorption is the "hydrophobic" effect. Inasmuch as the magnitude of hydrophobic effects is known also to depend on hydrostatic pressure (Braganza and Worcester, 1986), the effects of hydrostatic pressure on the swelling phenomenon were investigated. A more practical reason for studying the effects of hydrostatic pressure on swelling processes in clays is that montmorillonites, which are related to vermiculites, are widely used in oil drilling muds where they are often subject to hydrostatic pressure.

EXPERIMENTAL DETAILS

The vermiculite crystals were from Eucatex, Brazil, and had a charge density of 1.3 monovalent cations per $O_{20}(OH)_4$ unit. The n-butylammonium form was prepared as described by Braganza *et al.* (1989). The crystals were swollen by leaving them for 24 hr in a solution of n-butylammonium chloride of known concentration at 7°C. The swollen gel resulting from this treatment was loaded into a 2-mm-thick quartz cell together with solution. The quartz cell was contained in a Zircal pressure cell designed for pressures as high as 2 kbar (Braganza and Worcester, 1986).

The whole assembly was mounted on a standard goniometer for alignment in the neutron beam. The experiments were carried out on the D16 long wavelength diffractometer at the Institut Laue-Langevin, Grenoble, France (Institut Laue-Langevin, 1986). The
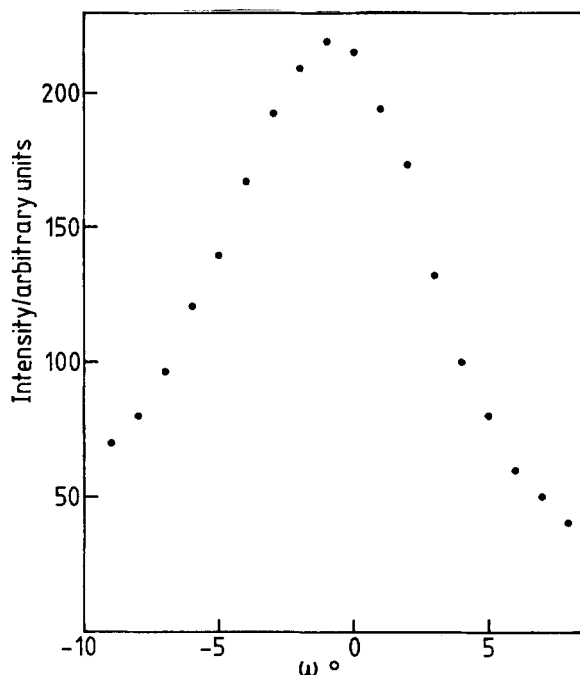
Figure 1.   Rocking curve on the first-order neutron diffraction peak of the swollen phase.

alignment of the sample, the method of temperature control, and the characteristics of the diffractometer are all described by Braganza *et al.* (1989).

For the calorimetric experiment a vermiculite sample previously fully exchanged with n-butylammonium vermiculite was rinsed with water and dried in an evacuated desiccator over calcium chloride. A known weight (about 1.5 g) was sealed in a calorimetric sample cell together with a known weight (about 3 g) of 0.06 M aqueous n-butylammonium chloride. The remaining space (about 0.5 cm³) in the cell was filled with air at atmospheric pressure. The experiment thus effectively gave the heat capacity at constant pressure. The calorimeter and its operation were described by Matsuo and Suga (1985).

RESULTS

n-Butylammonium vermiculite can exist in two states, which have been described as the crystalline state and the "osmotically" swollen state (van Olphen, 1977). The crystalline state contains a small amount of water and, within this state, several stable phases exist (Humes, 1985). The crystalline phase containing the largest amount of water has a c-axis spacing of 19.4 Å.

At ambient pressure, with an external concentration of 0.06 M n-butylammonium chloride, and at 9°C, the sample was in the "osmotically" swollen gel state. At this temperature three orders of the 00l reflection were observed corresponding to a c-axis spacing of 120 Å.
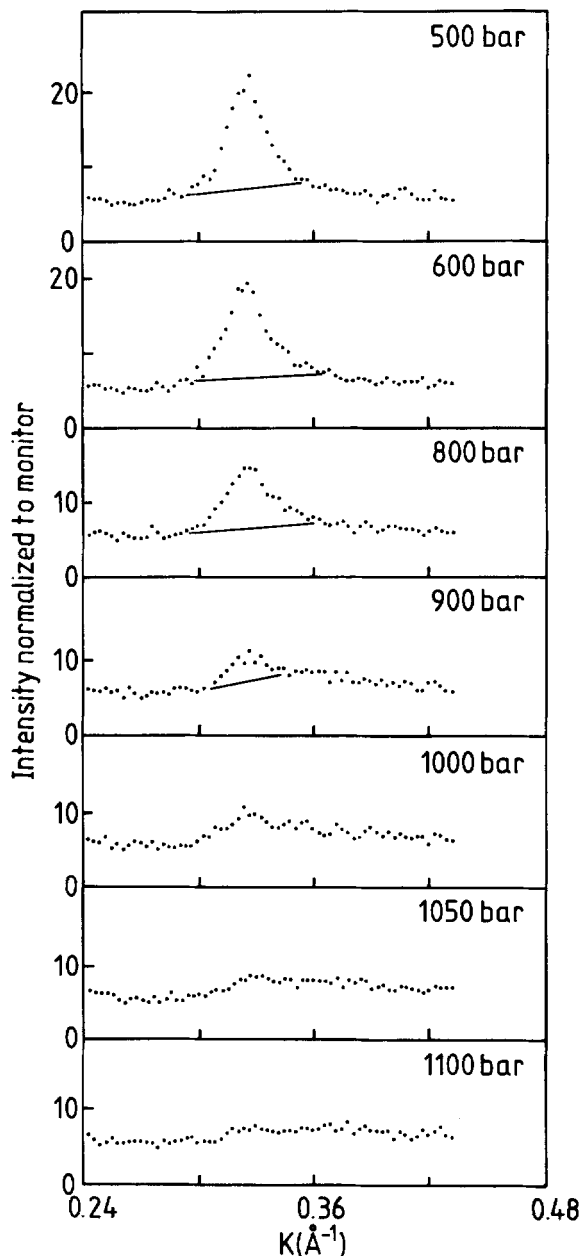

Figure 2.   Effect of pressure on the 00l reflection of the crystalline phase of n-butylammonium vermiculite at 20°C.

That the platelets in the gel remained well oriented after swelling was demonstrated by measuring the rocking curve on the 00l reflection. As discussed by Braganza *et al.* (1989), a rocking curve is a measure of the mosaic spread of the platelets. The curve obtained, shown in Figure 1, gave a mosaic spread of 5°–6°. The majority of the platelets were therefore oriented within an angular range of 5°–6°, a result similar to that obtained previously. The c-axis spacing also agreed with the results of Braganza *et al.* (1989). On warming the sample to 11°C the gel underwent a phase transition
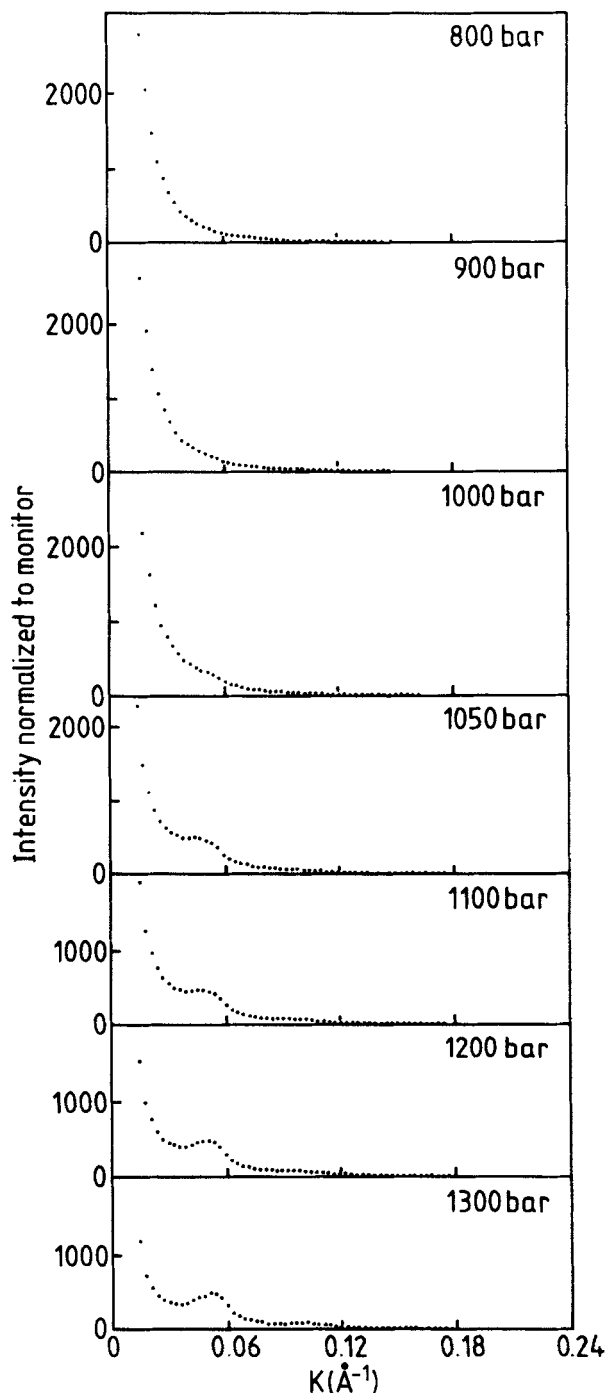
Figure 3. Effect of pressure on the low-angle diffraction pattern of n-butylammonium vermiculite at 20°C.

Table 1. Intensity of 001 reflection of crystalline phase of n-butylammonnium vermiculite in 0.1 M n-butylammonium chloride solution.

Pressure (bar)	Intensity (arbitrary units)
500	146
600	141
800	121
900	115
1000	81
1050	26
1100	~0

the scattering angle and λ the incident wavelength of the neutrons.

The initial measurement of the effect of hydrostatic pressure was made at 20°C, 9°C above the transition temperature to the crystalline phase at atmospheric pressure. With reference to the behavior of the first-order peak of the crystal at $\kappa = 0.325$ Å^{-1}, no significant change in this peak was noted as the hydrostatic pressure was increased to 500 bar. Above this pressure, however, the intensity of the peak decreased continuously as the pressure was increased. The diffraction patterns over the range 500 to 1100 bar, shown in Figure 2, indicate that the crystalline phase disappeared at about 1050 bar. The integrated intensities of the peak after subtraction of a flat background are given in Table 1. No further change was noted in this region of the diffraction pattern as the pressure was increased further to 2000 bar.

With reference to the change in the small-angle scattering as a function of pressure, no change in the pattern was detected as the pressure was increased to 800 bar. Only slight changes occurred between 800 and 1000 bar, but at 1050 bar the first-order reflection of the swollen phase appeared. At 1300 bar, first, second, and third orders of this reflection were observed. The patterns obtained between 800 and 1300 bar are shown in Figure 3, and the 1300-bar pattern is shown on an expanded scale in Figure 4. The integrated intensities,
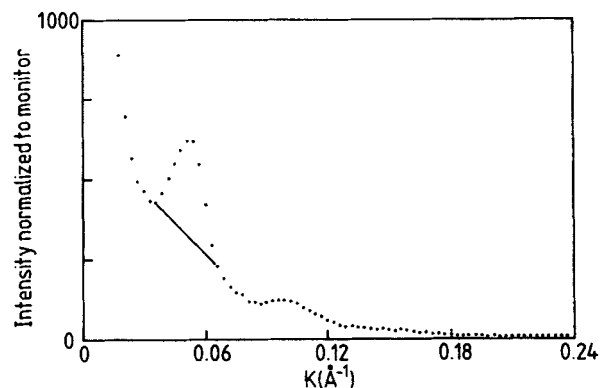

Figure 4. Small-angle scattering pattern of the gel phase of n-butylammonium vermiculite at 1300 bar and 20°C.

to a crystalline phase having a c-axis spacing of 19.4 Å. This transition was monitored by the growth of the first-order reflection of the crystalline phase at a value of the momentum transfer, κ, of 0.325 Å^{-1}, as described previously (Braganza *et al.*, 1989). The momentum transfer is defined as $(4\pi \sin\theta)/\lambda$, where 2θ is

Table 2. Intensity of the 001 reflection from the swollen phase of n-butylammonium vermiculite in 0.1 M n-butylammonium chloride.

Pressure (bar)	Intensity (001)	κ_{max} (Å^{-1})	d (Å)
1000	—	—	—
1050	501	0.0498	126
1100	665	0.0510	123
1200	889	0.0514	122
1300	1357	0.0516	122
1400	1542	0.0513	122
1600	1663	0.0521	121
2000	1788	0.0524	120

positions of the reflection, and the corresponding c-axis spacings are given in Table 2. As the pressure was increased further to 2000 bar, the c-axis spacing decreased by only about 1 Å per 300 bar, and the intensity of the first-order peak increased steadily over the whole range.

Thus, at 20°C, no crystalline material was detected at pressures >1100 bar, and no osmotic phase was detected at pressures <1000 bar. A narrow coexistence region at about 1050 bar was found, which we define as the transition pressure at this temperature. The transition was found to be reversible as the pressure was cycled between 500 and 1500 bar, just as it had previously been found to be reversible with respect to changes of temperature (Braganza et al., 1989). The rate of equilibration was surprisingly rapid, of the order of 10 min. The whole pressure cycle was then repeated at different temperatures. The resulting P-T phase diagram of the 40.1 M n-butylammonium system is shown in Figure 5.

Figure 6 shows the heat capacity of the swollen vermiculite per gram of dry mass. Points are shown for two series of measurements, and the good agreement between them confirms the reproducibility of the swelling transition. A peak in the heat capacity curve was noted at 10.1°C, which does not quite agree with the temperature estimated from the neutron diffraction data, i.e., about 15°C. This discrepancy almost cer-

Figure 6.   Heat capacity across the swelling transition of n-butylammonium vermiculite (per gram of dry material) in 0.06 M solution of n-butylammonium chloride.

tainly resulted from the necessary use of a very small amount of solution in the heat capacity measurement. On swelling the vermiculite, the concentration of the small amount of solution present may have been altered by exchange of ions with the clay, which would then have caused a slight shift in the phase-transition temperature. Alternatively, the small amount of solution could have limited the final volume attained after swelling, again causing a shift in the transition temperature.

The enthalpy, ΔH, and entropy, ΔS, of the transition were calculated from the heat capacity curve by integration of the excess heat capacity, ΔC_p, and $\Delta C_p/T$, respectively. The normal heat capacities needed for the calculation were determined by interpolation of the heat capacities outside the transition region using the linear function

$$\Delta C_p/J \cdot K \cdot g = 9.438 + 0.00140T/K$$

The numerical coefficients were determined by the method of least squares. The following results were obtained:

$$\Delta H = 5.2 \pm 0.1 \text{ J/g}$$
$$\Delta S = 0.0183 \pm 0.0004 \text{ J/K} \cdot g.$$

DISCUSSION

Because the application of hydrostatic pressure caused the vermiculite to swell to its osmotic phase, the total volume of the gel phase was less than that of the crystalline phase and the appropriate amount of solution, even though the gel phase itself represented a five- to six-fold expansion of the crystalline phase. The effect was totally unlike that of uniaxial pressure along the
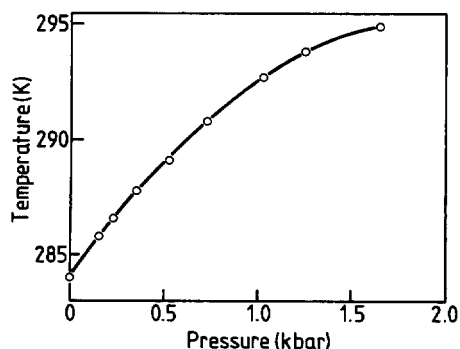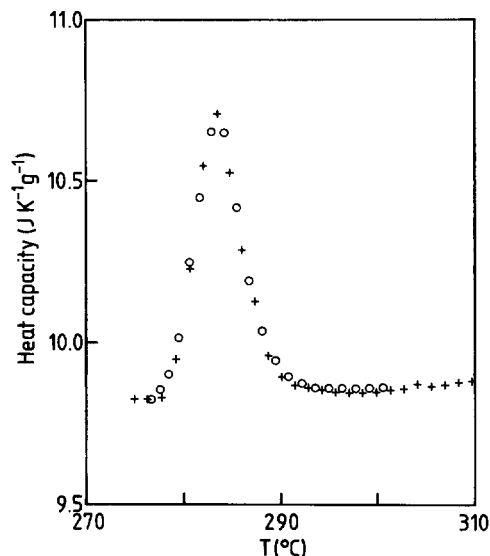

Figure 5.   Phase diagram for swelling of n-butylammonium vermiculite in water as function of temperature and pressure. Osmotic phase lies in lower half of the diagram.

c-axis, which caused a sharp decrease in the d-value of the gel phase and eventual transformation to the crystalline phase (Rausel-Colom, 1964).

These results were somewhat unexpected and give important information about the nature of the solution between colloidal particles. dP/dT along the phase boundary was determined from Figure 5, and is related to the entropy and volume changes of the phase transition by the standard equation:

$$dP/dT = \Delta S/\Delta V.$$

dP/dT was approximately constant at low applied pressures at 85 atm/K ($\equiv 8.5 \times 10^6$ J/m$^3 \cdot$K). The entropy of the transition was 0.0183 J/K·g of dry clay at 10.1°C. The combination of the two values gave a volume change for the transition of -2.15 cm^3/kg of dry clay. Because the density of the vermiculite is about 2.3, this volume change corresponds to a contraction of 4.9 cm^3/liter of dry clay for a five- to six-fold expansion. If this contraction is converted to a change in the water volume from the bulk solution to between the clay plates, it is equivalent to a fractional decrease of slightly less than 0.1%. Such a contraction would have been difficult to observe directly because swelling of the crystals commonly caused the release of air bubbles, which were presumably trapped at an unknown pressure during the formation of the material.

The reversibility, sharpness, and reproducibility of this unusual phase change from crystalline to swollen gel show that it is a true thermodynamic transition. In DLVO theory, 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 change between crystalline and swollen phases is therefore not possible within the framework of DLVO theory. Additional short-range repulsive force, which modifies the relative depths of the two potential minima, e.g., a hydration force (Low, 1987), must therefore be introduced. Serious discrepancies between the DLVO theory and observations of clay swelling have sometimes been attributed to possible imperfections in the clay materials themselves (see, e.g., Hunter, 1987). The

sharpness of the phase transition observed here suggests that imperfections do not play a part in the swelling process of the vermiculite.

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