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NEUTRON DIFFRACTION STUDIES ON LITHIUM MONTMORILLONITE-WATER DISPERSIONS

Key Words—Dispersion, Montmorillonite, Neutron diffraction, Surface area.

INTRODUCTION

The separation of a colloidal dispersion, under certain conditions, into an ordered phase and a co-existent disordered phase has been well known for some time. The separation of rod-like particles of tobacco mosaic virus into two phases was reported by Bernal and Fankuchen (1937), and the arrangement of plate-like particles of β-FeOOH into parallel layers with uniform spacings of the order of the wavelength of visible light was first reported by Zocher (1925). In the latter system brilliant colors due to Bragg diffraction were noted in visible light and were called schiller layers. The separation of bentonite clays into two phases was reported by Langmuir (1938), but no measurements of the spacings in the ordered phase were reported. More recently Hiltner and Krieger (1969), Barclay *et al.* (1972), and Hachisu *et al.* (1973) clearly demonstrated that polystyrene lattices, which contain spherical particles with a narrow distribution of diameters, separate into an ordered phase which often exhibits brilliant iridescent colors and a coexistent disordered phase which has a characteristic milky appearance due to scattering. The ordering of the latex particles can be readily achieved by the addition of mixed-bed ion-exchange resin which reduces the bulk electrolyte concentration to a low value, usually of the order of 10^{-5} mole/dm^3 or less, for a 1:1 electrolyte such as lithium chloride.

In aqueous systems which show phase separation, the particle-particle interactions are dominated by electrostatic repulsive forces. Following Barclay and Ottewill (1970) and Cebula *et al.* (1979), it was likely that treatment of a Li-montmorillonite dispersion with an ion-exchange resin would lead to a separation into two phases and that the more concentrated phase would contain numerous arrays of parallel montmorillonite plates which could act as a Bragg diffraction lattice with a long d(001) spacing. It was also postulated from previous work (Cebula *et al.*, 1979), that these spacings would be within the range observable by small angle neutron scattering.

EXPERIMENTAL

The sample used was montmorillonite (A.P.I. 26) from Clay Spur, Wyoming, as prepared for the American Petroleum Institute Clay Minerals Standards Project No. 49. It was converted into Li-montmorillonite using lithium chloride solutions by the same procedures as previously described for the preparation of Na-montmorillonite (Barclay and Ottewill, 1970; Cebula *et al.*, 1979). The material was normally prepared for use as a 2% (w/v) dispersion of Li-montmorillonite in 10^{-3} mole/dm^3 lithium chloride.

Examination of the Li-montmorillonite by electron microscopy showed that it was dispersed as single platelets. Consequently, the system was monodisperse with respect to plate thickness, with a dimension of ~10 Å. The width and breadth of the platelets, however, varied from ~0.2 μm to 0.7 μm.

Mixed-bed ion-exchange resins were cleaned before use by the procedures described by van den Hul and Vanderhoff 1970. The clay was treated with the ion-exchange resins in quartz tubes 25 cm long and 1 cm internal diameter which were thoroughly washed and steamed before use. The stock dispersion of 2% Li-montmorillonite was centrifuged to form a gel phase in the bottom of a tube, and the supernatant was removed. Dispersions of various approximate concentration were prepared from the gel and placed in the quartz tubes. Approximately 1 cm of mixed-bed ion-exchange resin was added to each tube, and the tubes were filled nearly to the top with dispersion. The tubes were firmly stoppered and immersed in a water thermostat at 25°C to within 1 cm of their tops. For an initial clay concentration of ~2% or greater, two layers separated after about two weeks with a gelatinous layer at the bottom of the tube and a less turbid, free-flowing liquid layer at the top. The volume of the lower layer was greater, the higher the initial concentration of the clay.

The upper liquid layer was decanted from the tube and a portion of the lower layer transferred to a 1-mm path-length quartz cell for neutron scattering examination. The concentration of solid in the lower layer was determined by drying an aliquot to constant weight at 100°C.

The neutron diffraction examination of the samples was carried out on a small angle diffractometer D11 at the Institut Laue-Langevin, Grenoble. An incident neutron wavelength λ of 15 Å was used, with a wavelength spread ($\delta\lambda/\lambda$) of ~10%. A two-dimensional multidetector was placed at a distance of 10.53 m from the sample, and enabled measurements to be made over a Q range of approximately 1×10^{-3} to 1.5×10^{-2}/Å, where $Q = (4\pi/\lambda)(\sin(\theta/2))$, with θ = the scattering angle. The dimensions of the sample exposed to the beam were about 5 mm × 10 mm. Satisfactory counting statistics were achieved after irradiation for approximately 20 min.

The basic diffractometer data were obtained in the form of raw counts against radial displacement, r, from the incident neutron beam. Standard computer programs (Ghosh, 1978) were used to reduce the detector data to intensity as a function of Q. The solvent background was then subtracted and the results normalized by the incoherent scattering from a standard sample in order to correct for solid angle effects, detector efficiency, and absorption and to give the intensity of scatter as a function of Q, namely I(Q).

RESULTS

In previous work it was established by both small angle neutron scattering by Cebula *et al.* (1980) and electron microscopy by Middleton (1978) that with Li-montmorillonite in 10^{-3} mole/dm^3 lithium chloride, the major part of a montmorillonite sample is dispersed as single plates with a fundamental unit layer thickness of ~10 Å.

Corrected diffraction patterns obtained in the present work are shown in Figures 1 and 2 in the form of the natural logarithm of the scattered intensity, ln I(Q), against Q. Since the scattering angle θ can be related to the sample to detector distance D and the radial distance r of the detector cell from the beam center, Q is given by,

$$|Q| = (4\pi/\lambda)(\sin(\theta/2)) = (2\pi/\lambda)(r/D) \quad (1)$$

since $\sin(\theta/2)$ for the small angles involved is equal to $\theta/2$ and $\theta = r/D$. Consequently, from the Bragg equation for a first order reflection,

$$\lambda = 2d \sin \theta_m = 2d \cdot \theta_m \quad (2)$$

where θ_m = the angle at which a maximum occurs in the scattered intensity, i.e., a Bragg peak.

The interplanar spacing d is thus given by,

$$d = 2\pi/|Q_m| \quad (3)$$

where $|Q|_m$ = the value of Q corresponding to θ_m. In this con-

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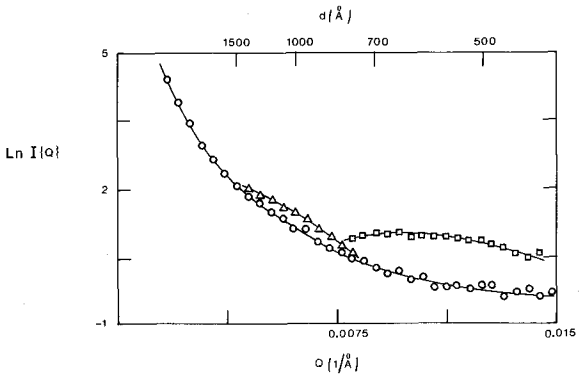


Figure 1. Small angle neutron scattering results from Li-montmorillonite dispersions: —○—, 2% w/v clay in 10^{-3} mole/dm³ lithium chloride solution; —△—, 2.0% w/v clay, ion-exchanged sample; —□—, 4.9% w/v clay, ion-exchanged sample.

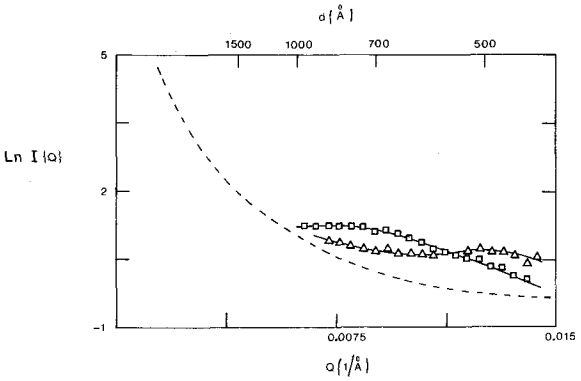


Figure 2. Small angle neutron scattering results from lithium montmorillonite dispersions: - - -, 2% w/v clay in 10^{-3} mole/dm³ lithium chloride solution; —□—, 4.3% w/v clay, ion-exchanged sample; —△—, 6.8% w/v clay, ion-exchanged sample.

text d is the equivalent basal spacing of the 001 reflection. The d scale corresponding to values of $|Q|_m$ is marked on Figures 1 and 2.

Five samples which had been subjected to ion-exchange treatment at different concentrations of montmorillonite were examined. One was also examined as a 2% w/v dispersion in 10^{-3} mole/dm³ lithium chloride. As can be seen from Figure 1 the scattering data obtained from this sample showed no significant Bragg effects. Hence, this sample provided a reference state against which the other samples were compared. The diffraction patterns obtained for the other samples clearly exhibit Bragg effects that are characteristic of structures with large basal spacings. The values of d obtained from the positions of the Bragg peaks are listed in Table 1.

DISCUSSION

In the presence of 10^{-3} mole/dm³ lithium chloride the small angle neutron scattering patterns obtained on 2% w/v dispersions of Li-montmorillonite showed no distinctive features and were consistent with the system containing a random arrangement of individual clay platelets. In the samples prepared by the addition of ion-exchange resin to lower the electrolyte concentration, peaks became apparent in the scattering patterns providing strong evidence that the montmorillonite plates had arranged into a parallel alignment with a long spacing between them which changed from 1200 Å in a 2% w/v dispersion to 450 Å in a 6.8% w/v dispersion.

The electrolyte concentration was not precisely known in the samples after ion-exchange treatment but was estimated from conductance measurements to be of the order of 10^{-5} mole/dm³. At this concentration of salt the reciprocal Debye-Hückel length is of the order of 1000 Å, and with the constant surface charge character of montmorillonite, long range electrostatic repulsion occurs between the plates. From direct measurements of the forces of interaction between montmorillonite particles Callaghan and Ottewill (1974) postulated in agreement with Norrish (1954) that electrostatic repulsive forces between plate surfaces controlled the behavior of montmorillonite gels at low electrolyte concentrations and that edge–face interactions were negligible. The present work lends support to this hypothesis and indicates that the strong repulsive forces between the faces of the particles orient the plates into a parallel alignment. It should be emphasized, however, that probably as a consequence of the polydispersity of the face sizes, the system exists with domains of ordered plates, rather than as a 'single-crystal' arrangement. Moreover, the polydispersity almost certainly contributes to the broadening of the Bragg peak, and it is anticipated that more monodisperse samples would give sharper diffraction effects.

To calculate the surface to surface distance between the plate faces, h, in a montmorillonite dispersion Barclay and Ottewill (1970) used the expression,

$$h = 2V/mA \qquad (4)$$

where V = the volume of liquid dispersion containing m grams of clay with a specific surface area of A. The latter value was taken as 800 m²/g corresponding to the crystallographically available area. The present experiments by small angle neutron scattering provide an opportunity to test this expression. The results obtained calculated on this basis are listed in Table 1 and compared with the d values obtained from the values of $|Q|_m$.

An alternative way of utilizing the small angle neutron scattering data is to obtain an estimate of the surface area of the montmorillonite in the dispersed state. For this purpose Eq. (4) can be rewritten in the differential form,

$$[\partial h/\partial(1/m)]_A = 2V/A \qquad (5)$$

and the gradient estimated from a plot of d (taken as equivalent to h) against 1/m, as shown in Figure 3. The value obtained in this manner was 885 ± 100 m²/g. This value indicates that the montmorillonite sample is fully dispersed under these conditions, a consequence of the strong electrostatic interaction, and that with sharper Bragg peaks, it would provide a method

Table 1. Estimation of interplate distances from small angle neutron scattering experiments and from specific surface area.

Clay concentration (g/100 cm³)	Interplanar spacing from small angle neutron scattering (Å)	Interplanar spacing from specific surface area[1] (Å)
2.0	1200 ± 80	1250
4.3	600 ± 40	581
4.9	550 ± 30	510
6.8	450 ± 25	368

[1] From A = 800 m²/g.

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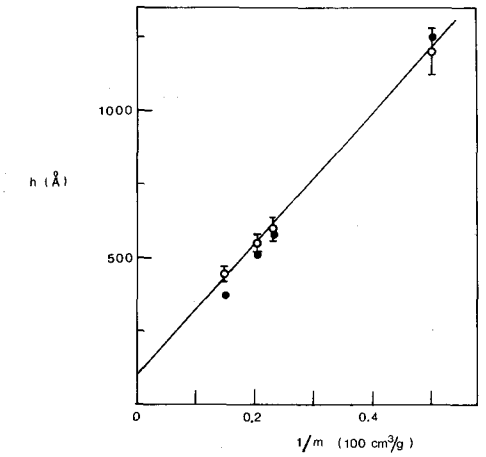


Figure 3. A comparison of interplanar spacings and their dependence on clay concentration: —○—, small angle neutron scattering results; —●—, from surface area, using Eq. (4), and taking the surface area as 800 m²/g.

of obtaining specific surface area values. Broadly it can be concluded that the previous method based on the use of Eq. (4) provides a reasonable estimate of h in concentrated dispersions.

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