X-RAY STUDY OF INTERACTIONS BETWEEN MONTMORILLONITE PLATELETS*

by

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ABSTRACT

SMALL angle X-ray scattering curves have been obtained for a series of Na Wyoming Bentonite clay samples containing 10% clay by weight and $NaPO_3$ in concentrations ranging from 0 to 100 meq/l. From the scattering data, the relative probability of spacings between parallel clay platelets was computed. For the sample containing no $NaPO_3$, the probability distribution showed a relatively broad maximum at an interparticle spacing of about 180 Å. As the concentration of $NaPO_3$ increased, the maximum became sharper and occurred for smaller interparticle distances. At $NaPO_3$ concentrations between 25 and 100 meq/l, the position d of the maximum was given approximately by the equation $d=21+18.4c^{-1/2}$, where d is in angstroms, and c is the $NaPO_3$ concentration in eq/l. The similarity of this relation to the dependence of d on the concentration of NaCl (Norrish and Rausell-Colom, 1963; Norrish, 1954) suggests that the interparticle spacing depends primarily on the sodium ion concentration and not on the concentration of the anion. The value of d appears to be independent of whether the gel was prepared by the method of Norrish and Rausell-Colom, in which a dried flake was allowed to come to equilibrium with an electrolyte solution, or whether, as in this investigation, the gel was obtained by centrifuging a dilute suspension. Since the Na ions act to reduce the double-layer repulsion between platelets, while the anions tend to be adsorbed on the platelet edges and thus reduce the edge-to-face linkages (H. van Olphen, 1962), the value of the most probable interparticle distance appears to be determined primarily by the magnitude of the double-layer repulsion, even though other properties of the clay gels, such as the rheological behavior, are governed mainly by edge-to-face attractions.

INTRODUCTION

THE purpose of the work described below was to use small angle X-ray scattering techniques to measure preferred equilibrium distances between parallel clay platelets in water with different electrolyte concentrations and to interpret the results in terms of the repulsive and attractive forces acting between the platelets.

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Similar studies have been performed earlier by Norrish (1954) and by Norrish and Rausell-Colom (1963). In their work, parallel ordering between the platelets was promoted by evaporating dilute suspensions on a glass plate and then equilibrating small lumps of the dried material with the desired electrolyte solutions.

From the X-ray scattering data, a distribution function can be calculated which indicates the probability of finding a platelet at a given distance from another platelet. In these distribution functions a maximum is observed, indicating a preferred distance between platelets. At this distance there must be a minimum in the net potential energy of interaction between parallel platelets. The results show that in general the preferred spacing decreases with increasing electrolyte concentration. This shift can be understood from the reduction of the double-layer thickness and the resulting decrease in the range of the double-layer repulsion between negatively charged plates as the electrolyte concentration is increased.

The nature of the attractive force which must compensate the double layer repulsion at the preferred equilibrium distance is somewhat obscure. Both Norrish (1954) and van Olphen (1962) have come to the conclusion that the van der Waals attraction is insufficient to account for the observed equilibrium distances and that probably the limiting factor in the process is cross linking of some of the particles by positive-edge to negative-face association. This conclusion is supported by the observation that the interparticle distances do increase when positive-edge to negative-face linking is reduced by reversal of the positive edge charge by adsorption of certain anions, such as the metaphosphate anion (Norrish and Rausell-Colom, 1963). However, the equilibrium distances in these phosphate-treated systems still cannot be explained satisfactorily from the combination of electrical double-layer repulsion and van der Waals attraction alone.

In the present work we have used sample preparation techniques different from the methods employed by Norrish and Rausell-Colom (1963). We have approached the equilibrium separation of the plates from the opposite direction by using an ultracentrifuge to concentrate dilute suspensions in electrolyte solutions of varying concentration. Also, in lieu of adding a small amount of metaphosphate to reduce edge-to-face linking and then varying the electrolyte content by adjusting the sodium chloride concentration, we have used only a series of concentrations of sodium metaphosphate. By this process we could study the effect of the sodium ion on the interaction of the double layers on the negative faces while simultaneously reducing the cross linking effect of the edge-to-face association by means of the metaphosphate anion.

EXPERIMENTAL METHODS

The Na-montmorillonite samples were prepared at Shell Development Co. laboratories, Houston, Texas, from Wyoming bentonite from Clayspur, Wyoming. A 2% distilled water suspension of Wyoming bentonite was passed through a Na^+ saturated Dowex 50 ion exchange column to convert the clay to Na-montmorillonite. After the quantity of sodium metaphosphate necessary to give the desired sodium metaphosphate concentration had been added to the 2% Na montmorillonite suspension, the sample was concentrated in an ultracentrifuge. The clay samples obtained directly from the ultracentrifuge were designated samples 2′ through 6′. The samples with higher sodium metaphosphate concentration had the highest clay concentration, because a higher concentration of sodium metaphosphate tended to break down more of the gel structure. A second series of samples, called samples 2 through 6, were obtained from the first series by diluting the more concentrated clay suspensions with the appropriate sodium metaphosphate solution until the resulting sample had a clay concentration of 10%. Sample 1 was a 10% Na-montmorillonite containing no sodium metaphosphate. The clay and sodium metaphosphate concentrations of the samples are shown in Table 1. All clay concentrations are expressed as grams of clay per 100 g of suspension.

TABLE 1.—COMPOSITION OF SAMPLES AND VALUES OF d AND L_1

Sample	Clay concentration %	$NaPO_3$ concentration (eq/l)	d (Å)	L_1(Å) (eq. 3)	L_1(Å) (eq. 4)
1	10.00	none	184	292	276
6	10.00	0.005	177	272	261
5	10.00	0.010	157	311	292
4	10.00	0.025	138	209	206
3	10.00	0.050	98	166	161
2	10.00	0.100	82	151	149
6′	11.51	0.005	137	214	213
5′	12.23	0.010	133	213	210
4′	13.26	0.025	105	148	145
3′	15.04	0.050	72	104	100
2′	16.53	0.100	73	144	145

The X-ray source was a copper-anode X-ray tube operated at a current of 16 mA and an average voltage of 24 kV. The scattered radiation was measured with a xenon-filled proportional counter with a built-in preamplifier, the output of which was connected to a linear amplifier—pulse height analyzer—scaler system. Wavelength selection was accomplished by pulse height analysis and a 0.00035-in.-thick nickel foil, which served as a β-filter. The high-voltage supply for the counter was a bank of dry cells with a voltage adjustable in steps. The X-ray collimation system has been described by Bale and Schmidt (1958).

The clay samples were studied in sample cells made by cutting a hole in a sheet of aluminum about 0.040 in. thick. The hole was sealed by two 0.00025-in.-thick Mylar plastic windows, one of which was cemented permanently to the cell with epoxy resin cement, while the other was attached with stopcock grease after the sample cell had been filled.

The sample cells were not completely filled, and a small air space was usually present above the sample. The Mylar windows caused little compression of the samples, which had a cross sectional area of about 0.5 × 3 cm, with the latter dimension being vertical.

Three different slit width settings were used to obtain each scattering curve. A slit width of 0.010 in. permitted measurement of the inner part of the scattering curve. The central part was studied with a slit width of 0.040 in. In order to obtain sufficient intensity in the outer portion of the scattering curve, the slits were widened to 0.070 in. The curves for each slit width extended over a sufficient range of angles to permit the three curves for a sample to be combined to form a composite curve.

At least 1000 counts were recorded in each intensity measurement, and the counting time was never less than 1 min. All data were corrected for background. The incident intensity was monitored periodically by measuring the scattering from standard samples at selected scattering angles. Intensity fluctuations were never greater than about 2% and usually were smaller.

The scattering curves were corrected for slit-height collimation errors (Schmidt, 1965). A modification of the method of Kratky, Porod, and Skala (1960) was used to correct for collimation errors resulting from the width of the slits.

ANALYSIS OF SCATTERING DATA

The data were interpreted in terms of a model described in an earlier study of montmorillonite clays in this laboratory (Hight *et al.*, 1962). In this model the sample is assumed to consist of n aggregates, with an average number N_0 of identical platelets per aggregate. Within an aggregate all platelets are assumed to be parallel, and the aggregates are considered to be randomly oriented with respect to each other, so that each aggregate scatters independently of the others. The thickness of a platelet is assumed to be small compared to its other dimensions. For this model, the scattered intensity $I(h)$ can be expressed (Hight *et al.*, 1962, eq. 7)

$$I(h) = nN_0F^2(h)i(h)$$

where

$$i(h) = 1 - 2(L_1)^{-1}\int_0^\infty dr[1-P(r)] \cos hr \tag{1}$$

and where $L_1 = L_0/N_0$, L_0 is the average value of the maximum separation of platelet centers within an aggregate, $F^2(h)$ is the scattered intensity from a single isolated randomly oriented platelet, $h = 4\pi\lambda^{-1} \sin(\theta/2)$, λ is the X-ray wavelength, θ is the scattering angle, and $P(r)$ is a function such that $2(L_1)^{-1}P(r)\,\mathrm{d}r$ is the probability that the distance from the center of a platelet to the center of another platelet has a value between r and $(r+\mathrm{d}r)$. [In eq. (1) the distribution function $P(r)$ is defined somewhat differently from the function $P(r)$ used by Hight *et al.* This difference in definition accounts for the slight difference between equation (1) above and equation (7) of Hight *et al.*]

By the Fourier integral theorem

$$P(r) = 1 - (L_1/\pi) \int_0^\infty \mathrm{d}h[i(h) - 1] \cos hr \tag{2}$$

Because the platelets have finite thickness, $P(0) = 0$, and thus by setting r equal to zero in (2), one obtains

$$L_1 = \pi \left\{ \int_0^\infty \mathrm{d}h[i(h) - 1] \right\}^{-1} \tag{3}$$

Also, from (1)

$$L_1 = 2[1 - i(0)]^{-1} \int_0^\infty \mathrm{d}r[1 - P(r)] \tag{4}$$

Equations (1), (2) and (3) are equivalent to equations used by Norrish and Rausell-Colom (1963). When $i(0)=0$, eq. (4) reduces to eq. (3) of Norrish and Rausell-Colom.

By numerical evaluation of the integral in (2), the distribution function $P(r)$ was calculated for each sample. Values of $F^2(h)$ were obtained by measuring the scattering from a 2% suspension of Na-montmorillonite in water. Previous measurements have shown that in the accessible range of scattering angles, in these suspensions the platelets scatter independently (Hight, Higdon, and Schmidt, 1960). The $F^2(h)$ curve in the present investigation was essentially identical to the curve given by Hight, Higdon, and Schmidt.

The $i(h)$ curves were found from the measured $I(h)$ and $F^2(h)$ curves by multiplying the latter curve by the constant which, within experimental error, made $F^2(h)$ coincide with the $I(h)$ curve for the larger scattering angles at which data were obtained. In order to minimize the error in this matching process, $P(r)$ was computed for the $i(h)$ curve obtained with the constant found by matching the $I(h)$ and $F^2(h)$ curves and also for $i(h)$ curves obtained for a series of constants differing by a few per cent from the first constant. The final value of the constant was chosen to be the value which made $P(r)$ most nearly equal to zero for r values near $r=0$.

The numerical integration was performed with an IBM 1710 computer, using a FORTRAN II-D program for numerical integration by Simpson's rule. Before the computer program was applied to the $i(h)$ curves from the scattering data, it was tested by assuming forms of $i(h)$ for which (2) could be evaluated both numerically and analytically and which also were roughly similar to the form of the experimental $i(h)$ curves. The tests investigated the effects of errors caused by the finite width of the increment in the numerical integration and by the fact that the scattering data extended neither to $h=0$ nor to infinite h. The results of these tests indicated that while there may be some uncertainty in $P(r)$ when r is less than the r value for the principal maximum in $P(r)$, the rest of $P(r)$ curve can be reliably determined from the scattering data. In particular, the position of the principal maximum in $P(r)$ appeared to be completely independent of all effects considered in the tests.

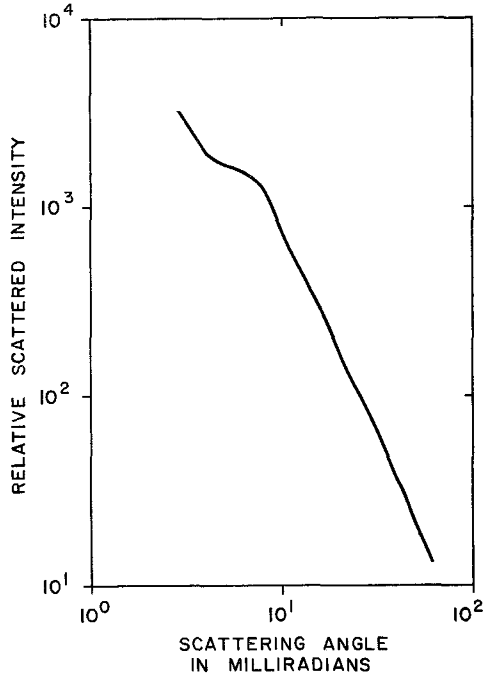

FIG. 1. The corrected scattered intensity for sample 1.

Typical $I(h)$ curves are shown in Figs. 1 and 2. Figures 3 and 4 give the $P(r)$ curves obtained from the $I(h)$ curves in Figs. 1 and 2, respectively.

Values of d, the position of the principal maximum of $P(r)$, are listed in Table 1, which also gives the L_1 values computed for each sample, both from equation (3) and from equation (4). The agreement of the two L_1 values for a given sample can be considered an indication on the consistency of the calculation of the distribution function $P(r)$. The quantity L_1, which is a normalizing constant used in developing the equations for analyzing the

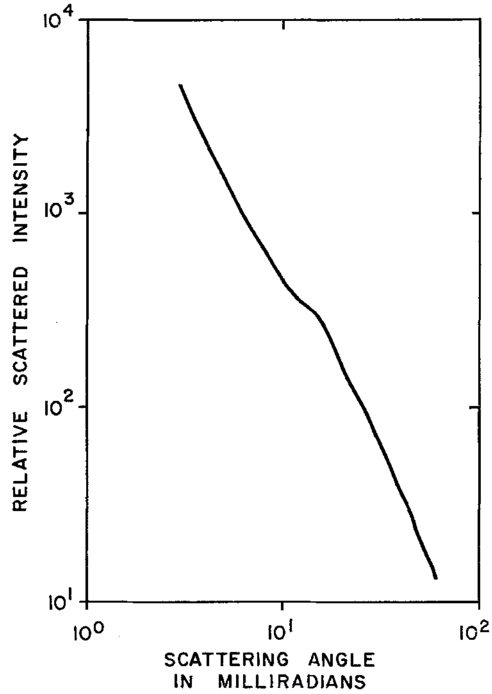

FIG. 2. The corrected scattered intensity for sample 2.

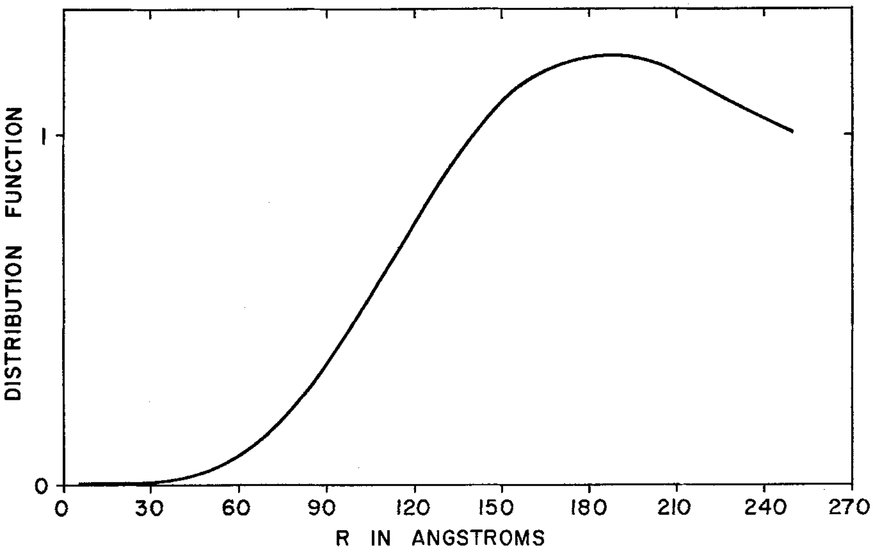

FIG. 3. The distribution function $P(r)$ for sample 1.

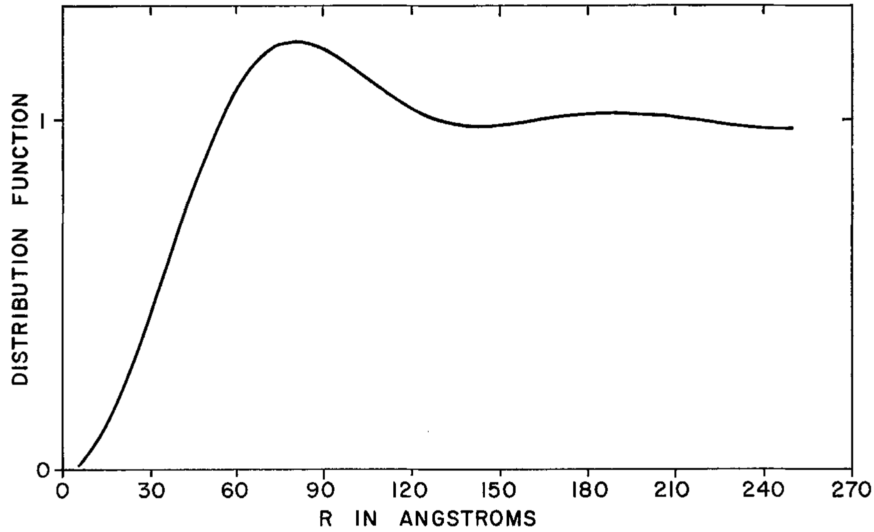

FIG. 4. The distribution function $P(r)$ for sample 2.

data, has no simple relation to d. Values of L_1 were computed primarily to check the numerical calculation. (Norrish and Rausell-Colom (1963) discuss the relationship between d and L_1.)

DISCUSSION

The d values of Table 1 are plotted in Fig. 5 as a function of $c^{-1/2}$, where c is the sodium metaphosphate concentration in eq/l. The results for samples 2′ through 6′ lie on one curve, while the d values in angstroms for samples 2 through 6 are on another curve which for $c^{-1/2}$ between $3(\text{l/eq})^{1/2}$ and $7(\text{l/eq})^{1/2}$ can be approximated by the line $d=21+18.4c^{-1/2}$. This line is very near the line $d=21+21.2c_0^{-1/2}$ which Norrish and Rausell-Colom (1963) found to describe the dependence of d on the sodium chloride concentration c_0 for Na-montmorillonite which had been treated with sodium metaphosphate. The two lines are drawn in Fig. 5, which also shows the line $d=21+10.1c_0^{-1/2}$ summarizing the spacings which Norrish and Rausell-Colom obtained for Na-montmorillonite treated with acid but not with sodium metaphosphate.

Since the dependence of d on the sodium chloride concentration (Norrish and Rausell-Colom, 1963) for clays pretreated with sodium metaphosphate is so close to the variation of d with sodium metaphosphate concentration in our experiments, the principal factor determining d is obviously the sodium ion concentration. In both series of experiments, the presence of the metaphosphate anion has the effect of reducing cross linking, thus permitting larger values of d than in the presence of NaCl alone. As before, it is still unsatisfactory to interpret the new data in terms of only the action of double-layer repulsion and van der Waals attraction. Possibly, some cross linking remains effective in the systems treated with metaphosphate, unless other, as yet unidentified, attractive forces are operative.

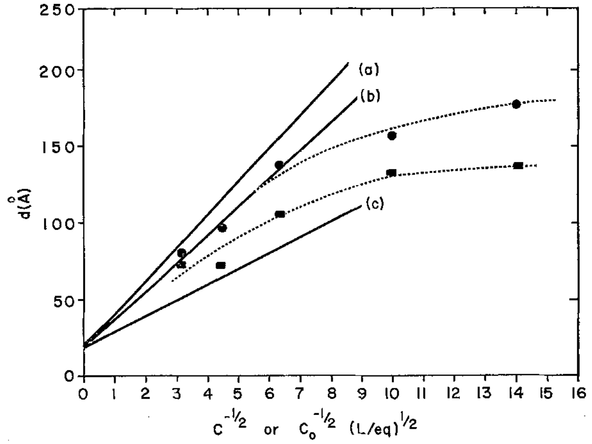

FIG. 5. Values of d spacings as a function of sodium metaphosphate concentration c. The d values for samples 2 through 6 and for samples 2′ through 6′ are indicated by circles and squares, respectively. Dotted curves are drawn through these points. Line (b) approximates the d values for samples 2, 3, and 4. The d spacings found by Norrish and Rausell-Colom (1963) for Na-montmorillonite samples with NaCl concentrations c_0 with and without Calgon treatment are shown by lines (a) and (c), respectively.

An average center-to-center platelet spacing d_{ave} can be computed for the clays by assuming that all platelets have a thickness 10 Å and a density 2.8 g/cm^3 (Hight, Higdon, and Schmidt, 1960) and that they are parallel to each other and are suspended in a medium with a density of 1.0 g/cm^3. For a clay concentration of 10%, $d_{ave} \simeq 260$ Å. The result that d_{ave} is greater than the d values of Table 1 is consistent with the assumption of aggregates in which the spacing between platelets is less than the average spacing for the sample.

The model used to obtain equations (1) through (4) assumes that the aggregates are randomly oriented and that all platelets within an aggregate are parallel to each other. While these assumptions probably are not perfectly satisfied in montmorillonite samples, a quantitative estimate of the effects of violation of these assumptions would be difficult. Probably the best justification for using these equations is that they have given reasonable results in several investigations (Norrish, 1954; Norrish and Rausell-Colom, 1963; Hight *et al.*, 1962). Porod (1948), in his discussion of the small angle

X-ray scattering from a single platelet, has shown that the scattered intensity is appreciable only when the platelet is oriented to act as a reflecting plane for the incident and scattered rays, so that these rays make equal angles with the normal to the plane. One thus might expect that the distribution function $P(r)$ would neglect any platelets that are bent or not parallel to the majority of the platelets in the aggregate. Since the scattered intensity from an aggregate is appreciable only when the platelets in the aggregate are oriented to act as reflecting planes, non-random orientation of the aggregate would affect only the magnitude of the scattered intensity and would be expected to have little influence on the calculated values of $P(r)$, which are obtained from the relative scattered intensity.

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