

LOW-ANGLE X-RAY DIFFRACTION STUDIES OF THE SWELLING OF MONTMORILLONITE AND VERMICULITE

by

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ABSTRACT

Various workers have studied the mechanism of swelling of Na-montmorillonite and have demonstrated that its ability to swell is due to water penetrating between the individual silicate sheets. In the present study intracrystalline swelling was followed by diffraction techniques which enabled the movement of the silicate sheets with respect to one another to be measured as a function of electrolyte concentration, with or without an externally applied load. The observations have been made on oriented flakes of Na-montmorillonite and single crystals of Li-vermiculite.

Qualitatively the minerals behave similarly when swollen in salt solutions. They both show an initial stage of crystalline swelling, after which there is an explosive increase to the gel state, and then the distance apart of the silicate sheets increases linearly with $C^{-\frac{1}{2}}$, where C is electrolyte concentration. Quantitatively, however, their swelling is very different, particularly after the "explosion", where vermiculite generally gives higher spacings than montmorillonite. There are two other important differences in the swelling of montmorillonite and vermiculite. Firstly, while the swelling of vermiculite appears to be reversible both with respect to electrolyte concentration and applied pressure, the swelling of montmorillonite shows a marked hysteresis. Secondly, in montmorillonite, swelling depends very strongly on pH or chemical treatment.

There is little doubt that the development of diffuse "double layers" gives rise to repulsive forces, which cause the silicate sheets to move apart. Van der Waals' forces have been regarded as providing attraction, but it is found that, at the observed inter-layer separations, the magnitude of these attractive forces is inadequate to balance repulsion, both in montmorillonite and vermiculite.

The present results demonstrate that in vermiculite swelling proceeds until the inter-layer separation causes the repulsion between sheets to drop to a value of $\sim 2.5 \times 10^4$ dyn/cm². This attractive force, which limits swelling, appears to be independent of sheet separation and electrolyte concentration. In montmorillonite swelling is opposed by edge-to-face bonds between sheets, whose number and strength can be controlled by chemical treatment. These bonds act to resist any displacement of the sheets, either swelling or contraction. This mechanism is compatible with the observed swelling behavior of montmorillonite, and explains the differences between the swelling of this mineral and that of vermiculite where, because the sheets are considerably larger, the force arising from edge-to-face bonds is small or absent.

INTRODUCTION

The low-angle diffraction studies of Norrish (1954), Foster, Savins and Waite (1955), and Rausell-Colom (1958) have demonstrated in a fairly direct

way that, when Na-montmorillonite swells to form a gel, it does so by water entering between the individual silicate sheets. After expansion the silicate sheets of each crystal are more or less evenly spaced and remain approximately parallel, it being this characteristic which makes it possible to study the gel structure with X-rays.

The above authors have measured the silicate layer separations as a function of water content and salt concentration. Their results are in substantial agreement, and may be summarized as follows: In the absence of electrolyte the interlayer spacing of Na-montmorillonite gels is directly proportional to water content, and the interlayer water accounts approximately for the water content of the gel. Electrolyte restricts the swelling in such a way that the interlayer separation is proportional to $C^{-\frac{1}{2}}$ (for $C < 0.3N$), C being the concentration of the solution. At greater concentrations than $0.3N$ the basal spacing is small, about 20 \AA (interlayer separation about 10 \AA). Li-montmorillonite and freshly prepared H-montmorillonite behave in a similar manner to Na-montmorillonite, but, if the mineral is saturated with other monovalent cations or with polyvalent cations, the interlayer swelling is restricted to a basal spacing of less than 20 \AA .

There is much evidence from measurements of swelling pressure (Bolt, 1956; Warkentin and Schofield, 1960; Aylmore and Quirk, 1962), negative adsorption (Schofield, 1947), etc., to indicate that, where the clay is behaving as a gel (interlayer separations greater than 30 \AA), there are repulsive forces between opposing silicate sheets due to the development of electrical diffuse Gouy layers. Since the clay does not swell indefinitely, the observed interlayer spacings represent the positions at which the repulsion is balanced by an opposing force. Norrish (1954), using his measured interlayer spacings, compared this repulsive force with the attraction to be expected from van der Waals' forces, and the agreement was poor, the repulsive force being many times greater than the attractive force. Rausell-Colom (1958) observed a marked hysteresis in the interlayer swelling in salt solutions, and to account for this behavior he postulated that double layer repulsion is opposed by resistive forces originating from edge-to-face bonds, a concept which had been used previously to account for the viscosity behavior of clay gels (Van Olphen, 1956) and their flocculation characteristics (Van Olphen, 1951; Schofield and Samson, 1954). The present study is aimed at obtaining a better understanding of the forces acting between particles in clay gels.

Vermiculite is very similar to montmorillonite in many respects, and for some time it has been known (Walker and Milne, 1950; Norrish, 1954) that single crystals of Li-vermiculite swell greatly in water. Recently, Walker (1960) showed that, in swelling macroscopically, vermiculite behaved similarly to montmorillonite, and the present authors, using Walker's material, were able to demonstrate that the interlayer separations in swollen vermiculite were very large (several hundreds of Angströms). Vermiculite was included in the present study since its behavior could give some indication of the effect on swelling of particle size and surface density of charge, these being the two relevant differences from montmorillonite. There is also the

advantage that flakes of vermiculite are a close approach to single crystals and give better diffraction data, with fewer ambiguities in interpretation, than montmorillonite.

EXPERIMENTAL

Sample Preparation

Most of the measurements reported in the present study were made on Wyoming bentonite (from U.S.A.) and on vermiculite from Kenya. A few experiments were also performed with Volclay bentonite (Black Hills, South Dakota), Red Hill Fuller's earth (montmorillonite from Surrey, England), montmorillonite from Monte Tidinit (North Morocco), and nontronite from Spokane (Washington, U.S.A.). Cation-exchange capacities were determined by Sr saturating the clay (using SrBr_2), the Sr content being measured on the dry clay by X-ray spectrography. Br analyses were made in the same way to check that free salt was not present.

The montmorillonite specimens were Na-saturated by prolonged washing in 2N NaCl, and excess salt was removed by washing with water. Dilute suspensions of the clay in distilled water were passed through a Sharples supercentrifuge to select the particles with equivalent spherical diameters of $<0.1 \mu$. This fraction was divided into several portions, and the following chemical treatments were carried out:

- (1) Treatment of the clay suspension with 0.1N HCl (a few minutes at room temperature) in the presence of 2N NaCl. This was followed by repeated washing with 2N NaCl.
- (2) Treatment with 2N NaCl of pH 11, adjusted with NaOH, and finally washing with neutral 2N NaCl.
- (3) Treatment with a 0.1 percent solution of "Calgon" of pH 10, adjusted with NaOH, and subsequent washing with 2N NaCl.

All clay suspensions were dialyzed to eliminate excess salt, and oriented aggregates were prepared by evaporation of sufficient gel onto a glass slide to give clay films of about 0.01 g/cm^2 , pieces of which ($10 \text{ mm} \times 0.5 \text{ mm}$) were used for diffraction. Montmorillonites with treatments 1 and 2 were swollen in neutral NaCl solutions, the pH after swelling being ~ 6 . The clay with treatment 3 was swollen in NaCl solutions whose pH was adjusted to 10 with Na_2CO_3 .

Flakes of uniform thickness (0.05–0.1 mm) were cleaved from large pieces of vermiculite. Those which were free from defects were cut to a suitable size ($10 \text{ mm} \times 0.5 \text{ mm}$) and saturated with Li^+ by treatment for several months with 1N LiCl at 60°C , with weekly changes of solution. The flakes were dried on filter paper to remove excess salt, and stored dry.

Some aspects of the vermiculite's behavior are worthy of comment. It was found at the beginning of this work that the swelling of this mineral was very erratic, and results were not always reproducible. Part of this trouble was eventually traced to the method of saturation with Li. If very strong solutions of LiCl were used, the exchange proceeded so slowly that in any reasonable

time the mineral was not completely saturated. The use of weaker saturating solutions (1N LiCl) gave better results, but there still remained a variability which cannot be explained. It was sometimes necessary to try several flakes prepared in an identical manner before one was found which exhibited a good swelling behavior. The specimens varied in the percentage of elementary layers that expanded beyond 15 Å, the specimens selected being those showing no detectable 15 Å peak after swelling.

Low-angle Diffraction Measurements

A specially constructed diffractometer (Rausell-Colom and Norrish, 1962) was used to record the low-angle diffraction patterns from the swollen clays. Intensities of diffraction were recorded on a chart recorder or with a scaler, the detection being made using a scintillation counter and pulse height analysis. The diffractometer was designed also to measure the degree of orientation of particles in the specimens. CoK α radiation was used.

In all cases the diffraction measurements were made with the clay immersed in the appropriate electrolyte. Two types of specimen containers were employed. For measurements of orientation or diffraction, in which the application of an external load to the specimen was not required, the clay and solution were contained in thin-walled plastic tubes whose ends were sealed to prevent evaporation. For measurements involving the application of external loads, the clay was contained in an open rectangular cell with thin plastic windows. The flake was positioned on the bottom of the cell and pressure was applied from the top via a flat foot. The cell was sealed by a layer of Apiezon oil floating on the surface of the solution.

INTERPRETATION OF X-RAY DATA

The method of interpretation of the diffraction results was basically the same as that used by Norrish (1954), and consists of calculating the distribution function $W(R)$ from the expression

$$W(R) - 1 = \frac{d''}{\pi} \int_0^{\infty} i(\mu) \cos \mu R d\mu \quad (1)$$

where d'' is the average distance between silicate sheets (the determination of its value is discussed later), μ equals $(4\pi \sin \theta)/\lambda$, θ being the Bragg angle, and $i(\mu) = (I/\mathcal{E}F^2) - 1$, where I is the diffraction intensity in absolute units.¹ I is made absolute by making the curves for I/\mathcal{E} and F^2 coincide at large angles ($\theta \sim 4^\circ$). \mathcal{E} is the correction for the Lorentz and polarization factors. The

¹ The use of slit collimation of the X-ray beam in low angle diffraction techniques usually implies a distortion of the diffraction measurements (Guinier and Fournet, 1955, pp. 114 ff.) for which tedious corrections are necessary before interpretation can be made. However, this distortion is greatly reduced if specimens having preferred orientation are used (Rausell-Colom, 1962). With highly oriented specimens, i.e. vermiculite flakes, no correction is necessary, and for specimens of medium orientation the simple corrections derived by the above author have been made.

structure factor F_{00l} is calculated from the structure of a single 10\AA sheet of montmorillonite, making allowance for the electron density due to water in the interlayer space.

The distribution function $W(R)$ gives the probability of finding an elementary silicate sheet at a given distance from any sheet (as origin), the probability at very large distances being specified as unity. The main interlayer distance in the gel is given by the mode of $W(R)$. This spacing, d , is not necessarily the same as the average spacing, d'' .

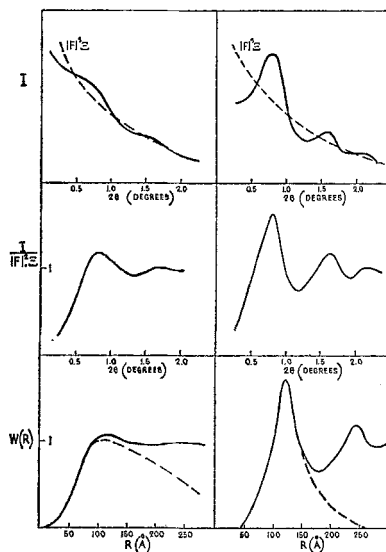


FIGURE 1.—Relationship between intensities of diffraction and distribution functions for a poorly ordered and a well-ordered specimen.

Figure 1 shows diagrammatically the interpretation of two idealized diffraction traces, having the same d , but one showing sharp and the other diffuse diffraction effects. The function $W(R)$ does not differentiate first, second, . . . , neighbors, and it is the relationship between adjacent sheets which is of most interest. In simple cases the nearest neighbor distribution function $F_1(R)$ can be derived from $W(R)$ (Rausell-Colom, 1958) and, for the two cases considered, $F_1(R)$ is shown in Fig. 1 in broken lines. Where $W(R)$ is sharp $F_1(R)$ is nearly symmetrical, and d'' will not be very different from d . In the case of the diffuse $W(R)$, $F_1(R)$ is broad and asymmetrical and d will be less than d'' .

Implicit in Eq. (1) is a knowledge of d'' ; this is obtained as follows: For $R=0$, $W(R)=0$, so that

$$-1 = \frac{d''}{\pi} \int_0^{\infty} i(\mu) d\mu$$

or

$$d'' = \frac{\pi}{\int_0^{\infty} i(\mu) d\mu} \quad (2)$$

If, following James (1948, p. 474), a function $\rho(R)$ is introduced, giving the density (number of layers per unit distance) at a distance R from any given layer, then

$$\frac{1}{2} + \int_0^{R'} \rho(R) dR = \rho_0 \cdot R'$$

ρ_0 being the average density, i.e. $1/d''$. R' is a large value of R , where $W(R)$ is constant with the value of unity, and therefore $\rho(R') = \rho_0$. The term $\frac{1}{2}$ is added since a sheet exists at the origin ($R = 0$) but this is not included in $\rho(R)$. Since $\rho(R) = \rho_0 \cdot W(R) = W(R)/d''$ it follows that

$$\int_0^{\infty} [1 - W(R)] \cdot dR = d''/2 \quad (3)$$

The values of d'' obtained from Eqs. (2) and (3) should coincide if the units of $W(R)$ are correct.

By definition, d'' is the arithmetic mean of $F_1(R)$,

$$d'' = \frac{\int_0^{\infty} R F_1(R) dR}{\int_0^{\infty} F_1(R) dR}$$

and, since $F_1(R)$ is obtained in the same units as $W(R)$, then

$$\frac{1}{d''} \int_0^{\infty} F_1(R) \cdot dR = 1 \quad (4)$$

and

$$\int_0^{\infty} R F_1(R) dR = (d'')^2 \quad (5)$$

The determination of $F_1(R)$ from $W(R)$ involves approximations which can make the profile of $F_1(R)$ uncertain at high values of R . Equations (4) and (5) can be used to check the correctness of $F_1(R)$.

The distribution of sheets in a swollen specimen can only be described adequately by $F_1(R)$. To describe swelling by a single parameter, d or d'' should be used depending on the purpose. Physical swelling will be proportional to d'' , assuming that intracrystalline swelling alone accounts for the swelling of the specimen, but if the separation of neighboring sheets is regarded as a stable position resulting from opposing forces, it is d which will correspond to the

minimum in the potential energy curve. It is for this reason that d is used in making the various calculations concerning forces.

If only d is required this can be found with sufficient accuracy by application of Bragg's law to the angle, 2θ , corresponding to the maximum of $I/(\mathcal{E}F^2)$. In most cases this function shows well-defined peaks with several orders of diffraction, whose maxima can be located accurately. In other cases, however, very diffuse peaks are obtained, and the error in locating the maxima is large. As $W(R)$ will also have a diffuse profile in these cases, it will be equally difficult to locate its maximum.

Since the diffraction patterns are obtained by setting the plane of the flake at an angle θ and the detector at an angle 2θ with respect to the direct X-ray beam, only those sheets whose inclinations, relative to the plane of the flake, lie within a certain angular range will be able to diffract. This angular range is determined by the dimensions of the reciprocal rod and, if sheets are regarded as rigid planes, it will be of the order of one degree, even for the smallest particles ($\sim 2000\text{\AA}$ diameter). However, electron optical (Bates and Comer, 1955) and electron diffraction studies (Cowley and Goswami, 1961) show that sheets are flexible and undergo bending. Thermal motion will undoubtedly contribute towards bending of the sheets. These distortions will increase considerably the above angle.

Two important implications, concerning the $W(R)$ and $F_1(R)$ functions, result from these considerations. Firstly, wedge-shaped structures will not be detected, because fairly inclined neighboring sheets will not diffract simultaneously. Secondly, slightly inclined sheets which diffract simultaneously will contribute to the diffuseness of $W(R)$ and $F_1(R)$, because their distance of separation is not constant.

Diffuseness in $F_1(R)$ and $W(R)$ may also represent a structure of parallel but irregularly spaced sheets.

RESULTS

Cation-exchange capacities of the vermiculite and montmorillonite used are given in Table I. Surface densities of charge, calculated from the exchange capacities and from the (total theoretical) surface areas of these minerals, are also shown.

TABLE I.—CATION-EXCHANGE CAPACITY AND SURFACE DENSITY OF CHARGE OF MONTMORILLONITE AND VERMICULITE USED

	C.E.C. (in meq/100 g o.d. clay)	$\sigma \times 10^{-4}$ (in e.s.u./cm ²)
Kenya vermiculite	143	5.8
Wyoming montmorillonite	90	3.05

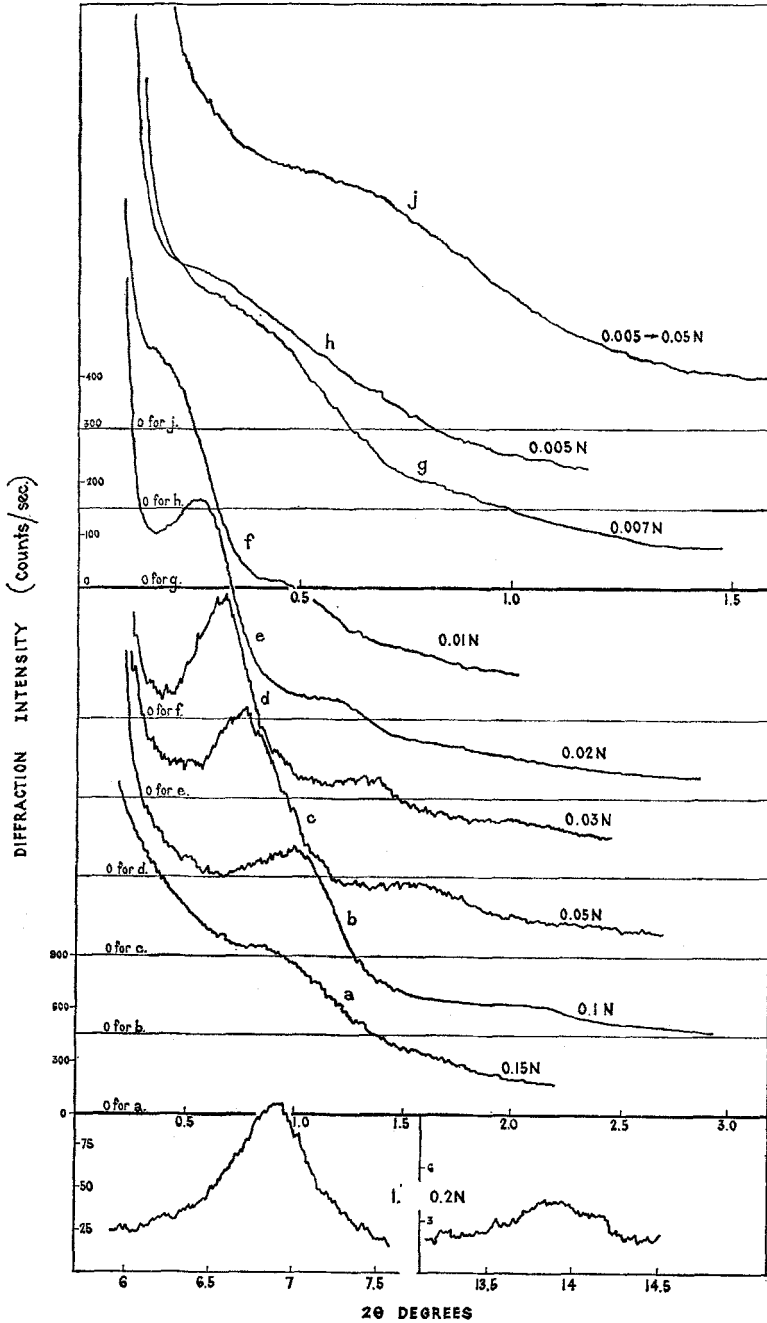


FIGURE 2.—Diffraction traces from Li-vermiculite swollen in LiCl solutions.

Figure 2 shows diffraction traces from vermiculite swollen in LiCl solutions of decreasing concentration. Except for the very dilute solutions, vermiculite gives relatively well defined diffraction peaks, and several orders are observable in the traces. The degree of orientation of particles was very good in all cases and changed very little with swelling. The orientation distribution for vermiculite swollen in 0.005 N LiCl is shown later.

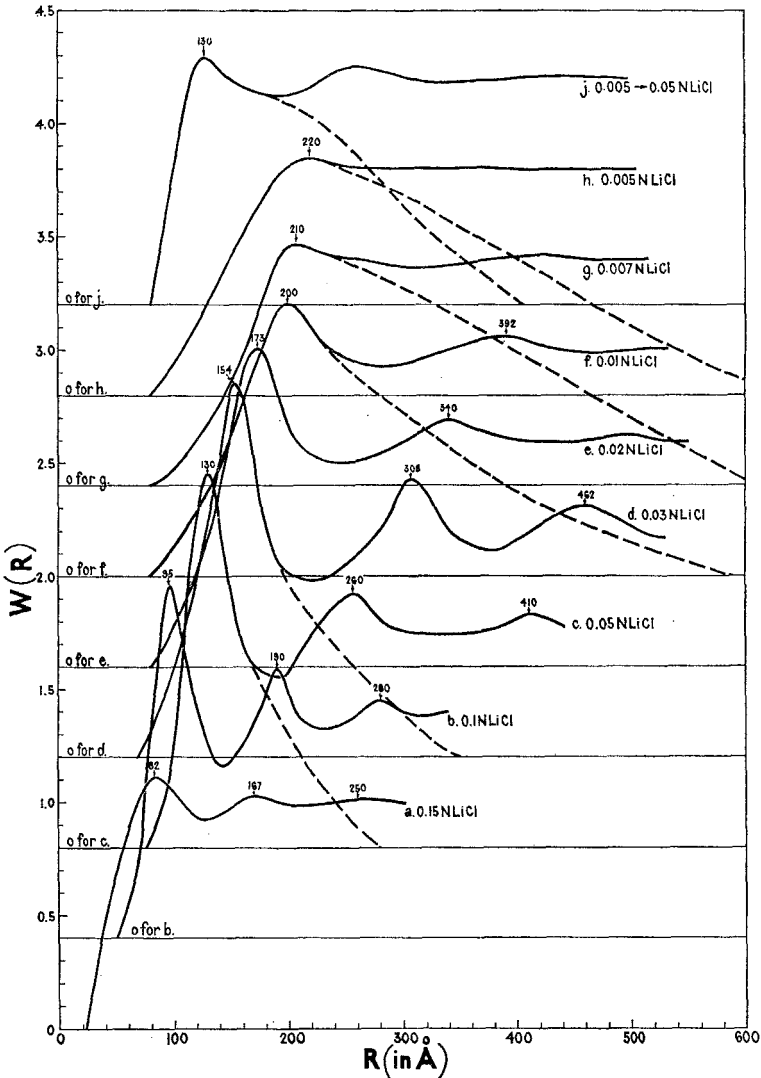


FIGURE 3.— $W(R)$ and in broken lines $F_1(R)$ for swollen Li-vermiculite specimens.

In Fig. 3 are the calculated distribution functions $W(R)$. The nearest neighbor distributions $F_1(R)$ were obtained from $W(R)$, and are shown in broken lines. Within the concentration range of 0.15N–0.02N the peaks in $W(R)$ are well resolved, and the corresponding nearest neighbor distributions (see curves c and d in Fig. 3) are sharp and only slightly skewed. For smaller concentrations than 0.02N the $F_1(R)$ distributions are markedly asymmetrical, and are spread over a wide range of distances. In Table 2 are given the interlayer distances d and d'' . It is seen that for the more diffuse distributions d'' is ~ 50 per cent greater than d .

Curve j of Fig. 3 shows $W(R)$ and $F_1(R)$ for a specimen of Li-vermiculite which was first allowed to swell in 0.005N LiCl, and afterwards was treated with a solution of 0.05N LiCl. When compared with $F_1(R)$ of a flake swollen directly in 0.05N LiCl (curve c in Fig. 3) it can be seen that the mode is the same but the distribution is broader. This difference is shown in the corresponding values of d'' , Table 2.

TABLE 2.—SWELLING OF LI-VERMICULITE IN LiCl SOLUTIONS. VALUES OF d (MODAL) AND d'' (ARITHMETIC MEAN) AS A FUNCTION OF CONCENTRATION

C (eq/l.)	d (Å)	d'' (Å)
0.050	130	154
0.030	154	180
0.010	200	269
0.007	210	300
0.005	220	304
0.005 \rightarrow 0.05	130	203

The swelling of vermiculite in solutions of LiCl, as a function of $C^{-1/2}$ (C being normality of the electrolyte), is summarized graphically in Fig. 4. For $C > 0.2$ N ($C^{-1/2} = 2.24$) the swelling does not progress beyond $d = 15\text{Å}$. Over a small concentration range in the region of $C = 0.15$ N the spacing of 15Å disappears, and there is a sudden expansion to 82Å , and then d increases continuously with dilution; initially it follows the line $d = 23.8C^{-1/2} + 22$, but, for concentrations below ~ 0.02 N ($C^{-1/2} = 7$) the increase in d with dilution gets progressively smaller, d tending towards a constant value of about 230Å for infinite dilution. This is in accordance with the observation that, even in water, vermiculite does not show unlimited expansion.

The data on physical swelling, included in Fig. 4 for comparison with the present results, was kindly supplied by Dr. G. F. Walker,¹ who has discussed the macroscopic swelling of Li-vermiculite (Walker, 1960; Garrett and Walker, 1962). The interlayer spacings reproduced here were calculated from thickness

¹ Chemical Research Laboratories, C.S.I.R.O. Melbourne, Victoria (Australia).

changes of flakes. Each experimental point represents the average of observations made on about twelve flakes, the individual results showing considerable scatter.

In Fig. 5 are reproduced several diffraction traces from vermiculite swollen under an externally applied load, and in Fig. 6 is shown the relationship between d and applied load for specimens swollen in 0.03N LiCl. For these experiments the maximum load was applied to the dry specimen, after which the electrolyte was introduced and the sample allowed to swell, and then its diffraction was recorded. The pressure was reduced by steps to zero, and then

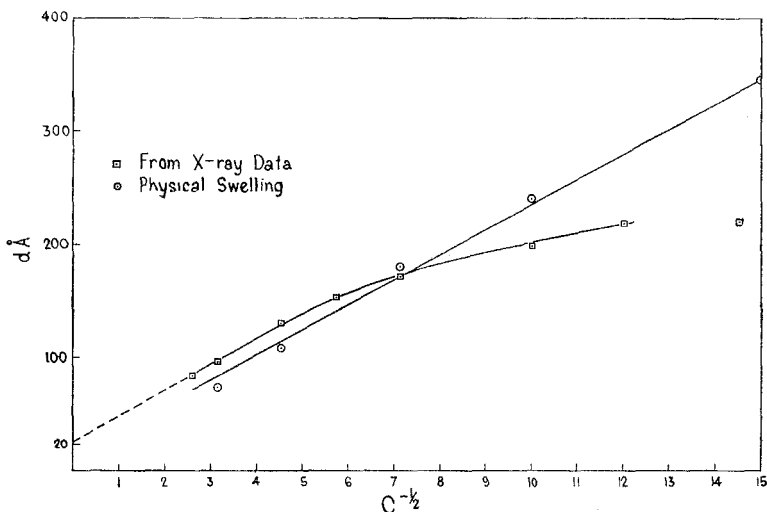


FIGURE 4.—Lattice expansion of vermiculite.

increased, so that a decompression-compression cycle was completed. Sufficient time (generally 30–60 min) was allowed after each change of pressure for the specimen to achieve equilibrium before the diffraction measurements were taken. It is seen that the application of a load sharpens the diffraction peaks [sharp $F_1(R)$], in some cases five orders being observable, and at the same time reduces d . The swelling is reversible, the spacing under a given load being the same whether it is approached from higher or from lower spacings.

Some diffraction traces obtained from swollen montmorillonites are reproduced in Fig. 7, and it can be seen that the peaks are much more diffuse than those of vermiculite. At an early stage of the work, when current results were compared with the earlier results of Norrish (1954) and Rausell-Colom (1958), it was realized that the degree of diffuseness of the diffraction from montmorillonite varied considerably. Since Wyoming bentonite was used in all cases, including the present, it was suspected that the differences arose from variations in preparation, and it was for this reason that the various chemical

treatments described above were used. A comparison of traces c and g of Fig. 7 shows that the diffuseness is associated with alkaline pretreatment of the clay. Calgon has the same effect as alkali. This dependence on preparation procedure

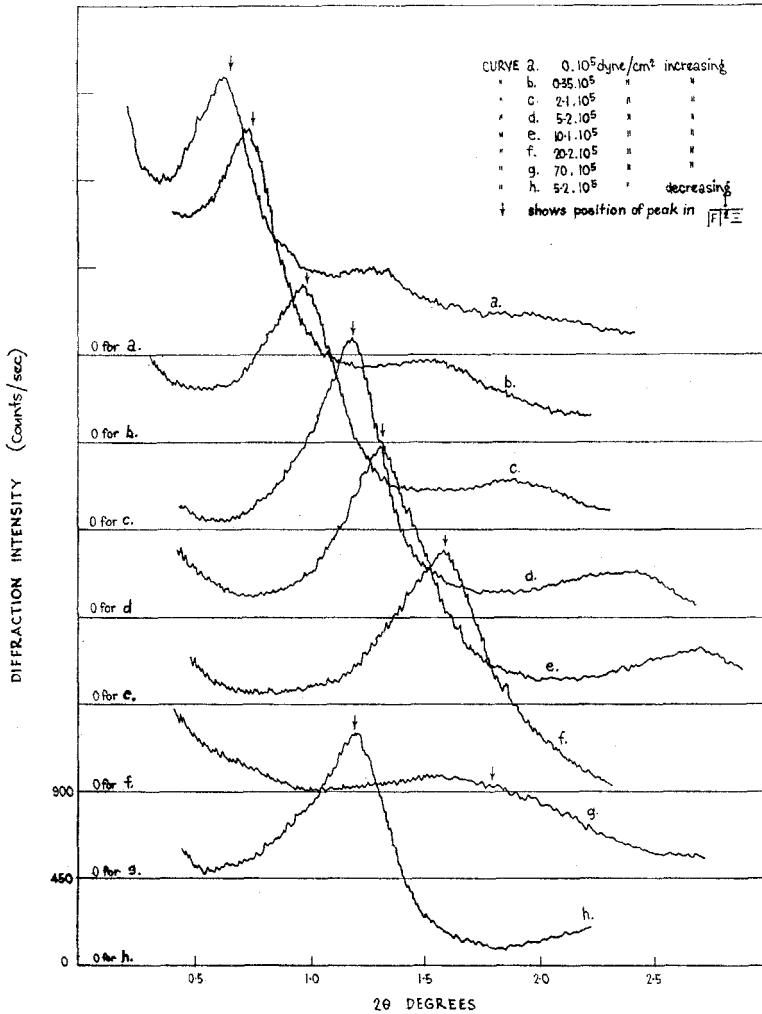


FIGURE 5.—Diffraction traces from vermiculite swollen under pressure in 0.03N LiCl.

accounts satisfactorily for the differences in the nature of the diffraction patterns. Rausell-Colom (1958) prepared his montmorillonite by Na-saturating with 2N Na-acetate (pH 9) and his patterns were relatively diffuse. The diffrac-

tion traces obtained by Norrish (1954) had more contrast, but the exact method used for Na-saturating the clay is not certain (it probably consisted of saturation with a neutral salt). Those of Foster, Savins and Waite (1955) show a high degree of contrast, and their samples were Na-saturated by neutralizing an acid clay.

Together with the diffuseness of the diffraction patterns, two other effects are associated with alkaline or Calgon treatment. The degree of orientation of particles in the swollen specimen becomes poorer, as shown in Fig. 8, and for the same concentration of electrolyte d is greater than in the acid-treated samples.

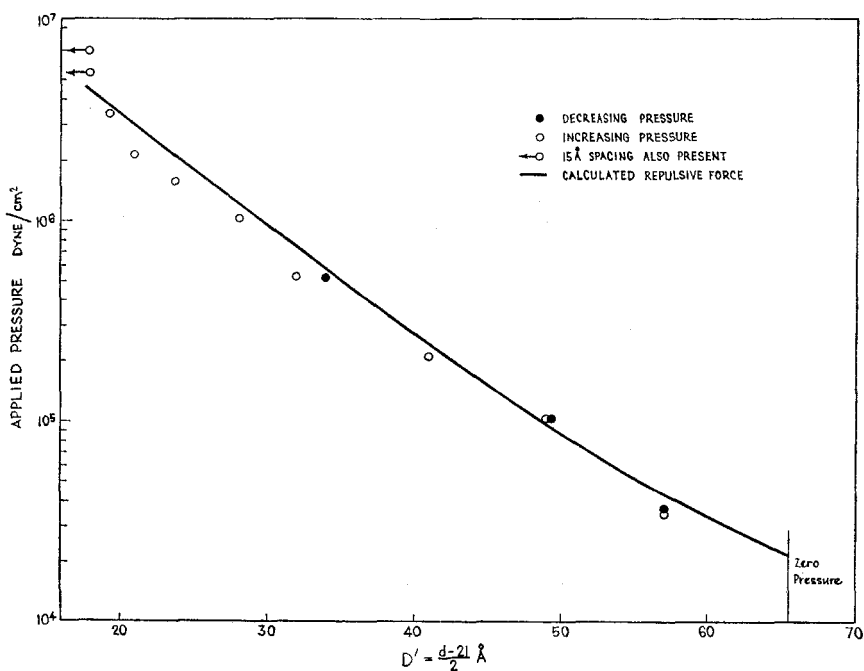


FIGURE 6.—Swelling of Li-vermiculite under pressure in 0.03N LiCl.

Although only a limited number of observations has been made on the treated montmorillonites, it is probable that the swelling, as dependent on electrolyte concentration, proceeds as shown in Fig. 9. Calgon-treated samples swell most, their swelling approaching that of vermiculite; acid-treated samples swell much less. Probably any degree of swelling between these limits can be achieved by an appropriate pretreatment. The earlier results of Norrish (1954) are in this category and are shown for comparison. It is possible that more drastic alkali or acid pretreatments could widen the upper and lower limits

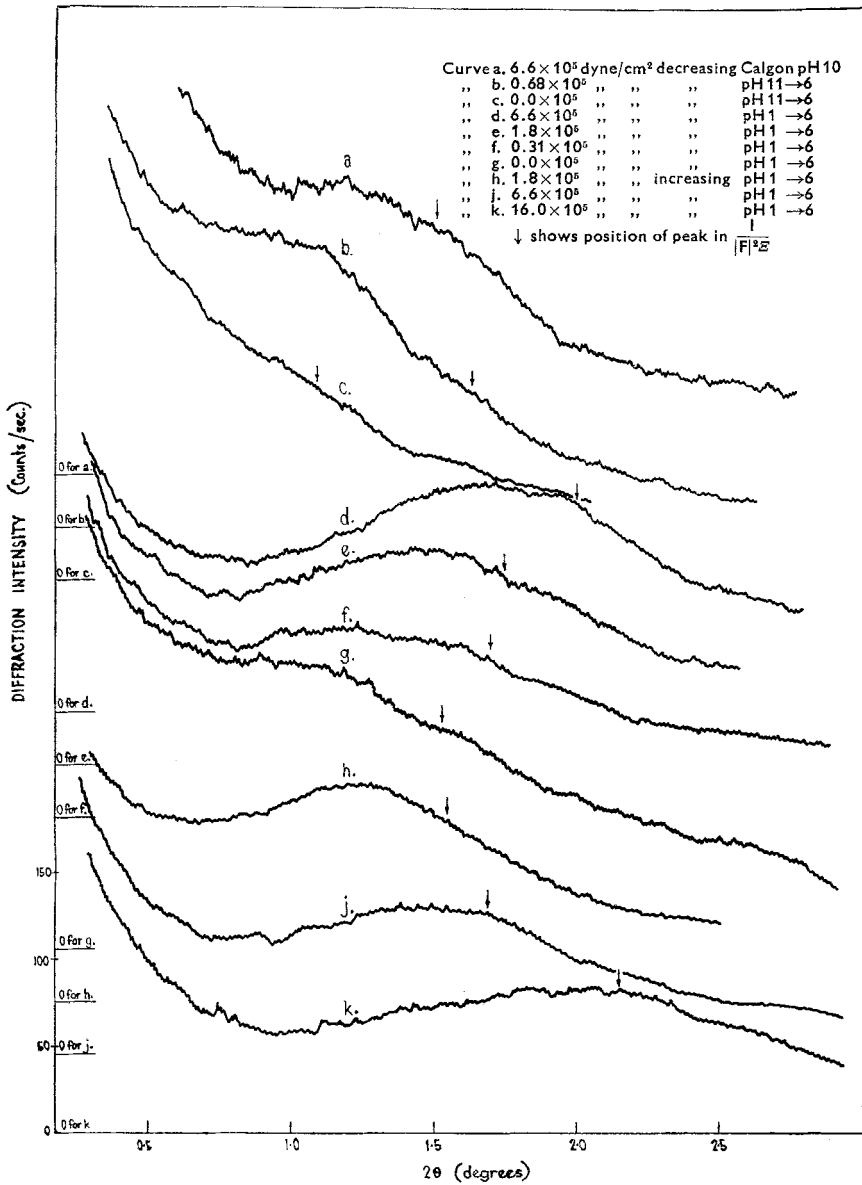


FIGURE 7.—Diffraction traces from montmorillonites swollen under pressure in 0.05 NaCl.

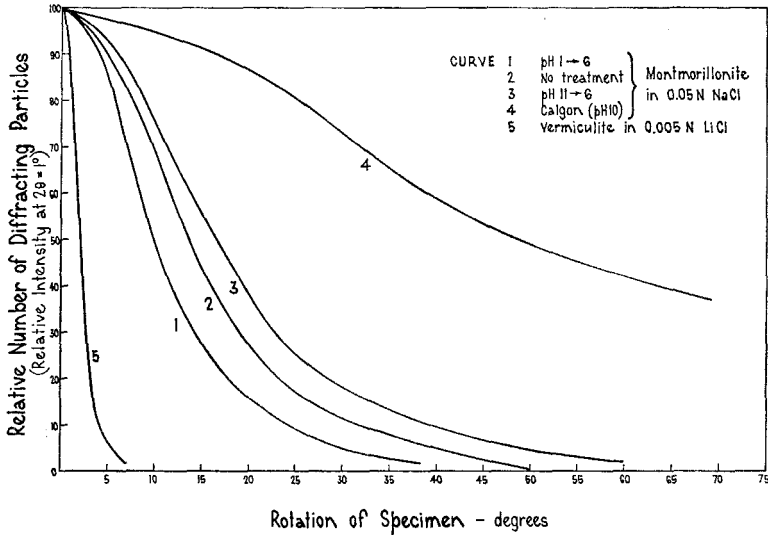


FIGURE 8.—Angular distribution of diffracting particles in swollen specimens of montmorillonite and vermiculite.

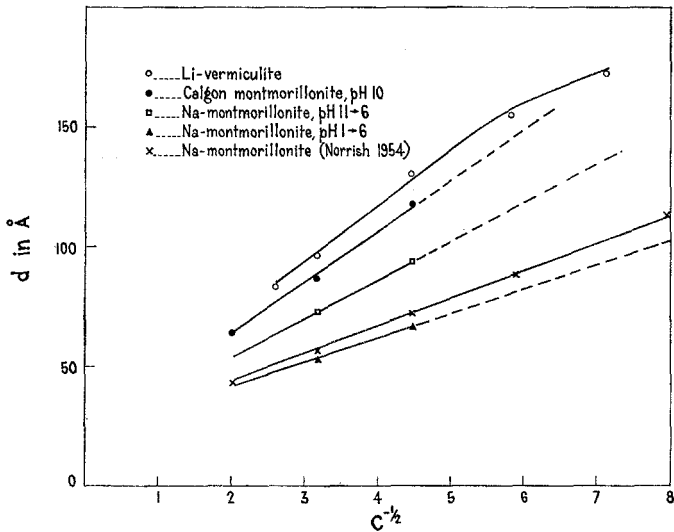


FIGURE 9.—Lattice expansion of pretreated Na-montmorillonites.

shown in Fig. 9. Despite the variations in swelling due to pretreatment, it appears that d remains an approximately linear function of $C^{-1/2}$, the slope of the line varying with treatment. The lines drawn in Fig. 9 correspond to

$$d = 21.2C^{-1/2} + 21 \quad \text{for Calgon treatment}$$

$$d = 16.1C^{-1/2} + 21 \quad \text{for alkali treatment}$$

$$d = 10.1C^{-1/2} + 21 \quad \text{for acid treatment}$$

and $d = 11.3C^{-1/2} + 21$ for the specimen used by Norrish (1954).

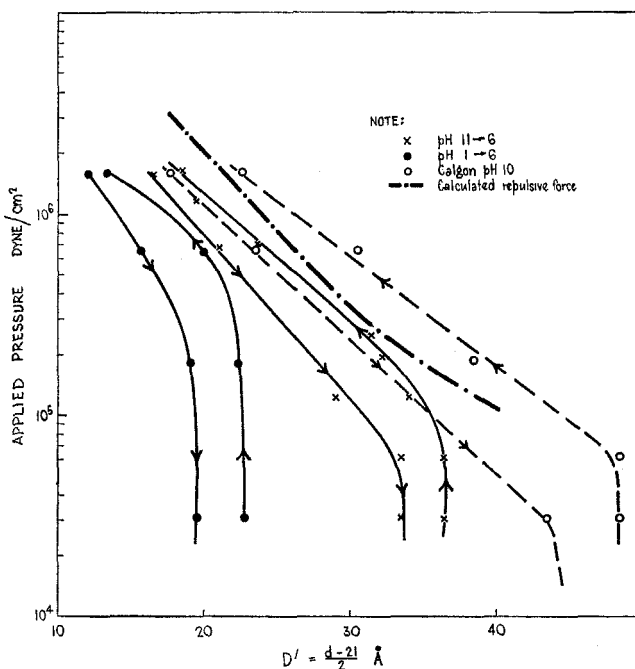


FIGURE 10.—Swelling of Na-montmorillonite under pressure in 0.05N NaCl.

Because the Calgon- and the alkali-treated samples were swollen in NaCl solutions of different pH, there may be some doubt as to how much of the increased swelling of the former is due to Calgon and how much is due to the higher pH. However, if Calgon-treated samples are swollen in neutral NaCl solutions, they behave more like the Calgon (pH 10) than like the alkali treated (pH 11→6) samples.

If it is remembered that, associated with the increase in d , $F_1(R)$ becomes more asymmetrical as diffuseness increases, then it is obvious that the average interlayer distance, d'' (i.e. physical swelling), increases considerably more than

is shown by Fig. 9. The physical swelling confirms this: the alkaline samples swell greatly and eventually begin to disperse. It is observed generally that when the degree of orientation worsens during swelling the flakes lose their coherency and tend to disperse.

When swollen against an external load, montmorillonite shows a marked hysteresis, and again the swelling is markedly dependent on chemical pre-treatment, as Fig. 10 shows. An interesting feature of this behavior is that, for loads up to a certain level, d does not change. However, the distribution is sharpened (curves g and h of Fig. 7) and so the average spacing (i.e. physical swelling) must decrease.

Some diffraction measurements were obtained from swollen montmorillonites from other localities, differing from Wyoming bentonite in exchange capacity, chemical composition and morphology. No systematic studies were made, but the nature of their diffraction traces indicates that swelling proceeds more or less in the same fashion as in Wyoming bentonite.

Some preliminary observations on the effect of particle size indicate that the fine fraction (0.1–0.3 μ) swells least and gives sharper diffraction patterns than the coarse fraction (0.3–2 μ), which gives very diffuse patterns and is less coherent and tends to disintegrate. In these respects the coarse particle size fraction, not treated with Calgon or alkali, seems to behave like the Calgon-treated fine fraction.

Results on one of the very fine fractions ($< 0.05 \mu$) showed that this fraction swelled more than the 0.1–0.3 μ fraction. However, this experiment was carried out with clay that received no other treatment than Na-saturation, and although the pH of the two fractions should have been comparable, there is no certainty that it was, and, since swelling appears to be very sensitive to pH, no definite conclusion can be drawn at this stage.

DISCUSSION

As mentioned earlier, Norrish (1954), assuming that the interlayer separations in montmorillonite gels represented the equilibrium position of sheets subjected to opposing forces, calculated the repulsion from the double layer equations and compared these values with the attraction due to van der Waals' forces, and found poor agreement. It is therefore worth considering briefly if the various assumptions used in the derivation of both these forces could alter their order of magnitude.

Double Layer Repulsion

The values for the repulsive force calculated by Norrish (1954) were obtained assuming that the surface density of charge of the montmorillonite sheets corresponded to complete dissociation of the exchangeable cations. In considering the discrepancy between double layer repulsion and Van der Waals' attraction van Olphen (1954) suggested that cations may be specifically adsorbed onto the clay surfaces, and that this could reduce the magnitude of the repulsion.

Although specific adsorption of cations has been postulated at times to explain the exchange properties of clays, there is little evidence to support the postulate that the normal exchangeable cations are bound by other than electrostatic forces. Structure determinations indicate that, before diffuse double layers are formed, ions lie midway between the silicate sheets and are coordinated with water molecules (Mathieson and Walker, 1954). Almost certainly, as swelling proceeds, more water will be coordinated around the ions, and with two or more shells of water between the ion and the silicate surface it is difficult to see what type of bond could give rise to the required specific adsorption. In a recent discussion van Olphen (1961) has considered the implications of his earlier postulate, and concluded that chemisorption of the cations is unlikely.

The simple equations that are normally used in calculations concerned with the double layer are based on a number of idealizing conditions, mainly centered around the acceptance of ideal behavior of the ions. Factors such as polarization energy of the ions, dielectric saturation of the medium, coulombic interaction, and short range non-coulombic interaction between ions, which, when introduced independently, could strongly affect these calculations, have been considered simultaneously by Bolt (1955). He concluded that, for colloids of a charge density not exceeding 2×10^{-7} meq/cm² (σ for montmorillonite and vermiculite are within this limit), these effects tend to offset each other, and that equations derived from the simple theory are adequate, despite approximations, in predicting the ionic concentration in the central plane between interacting particles. The good agreement between theory and experiment in measurements of swelling pressure (Warkentin and Schofield, 1960) and negative adsorption (Schofield, 1947) supports Bolt's conclusion that little would be gained by more elaborate treatments.

Accordingly, in the present study, repulsive forces p have been calculated for the particular experimental values of charge density, electrolyte concentration and interparticle distance (with dielectric constant $\epsilon = 80$, i.e. the value for liquid water), using the simple double layer equations,

$$p = 2nkT(\cosh u - 1)$$

$$\int_z^u (2 \cosh y - 2 \cosh u)^{-1/2} dy = -\kappa D'$$

and

$$\sigma = (n\epsilon kT/2\pi)^{1/2}(2 \cosh z - 2)^{1/2},$$

for $0 < u < 1$, where the meanings of the different variables are those defined by Verwey and Overbeek (1948, p. 22), or else, when the values of $\kappa D'$ are sufficiently large, the formula for small interaction

$$p = 64nkT\gamma^2 \exp(-2\kappa D')$$

has been taken as a good approximation.

In these calculations D' is taken as $(d-21)/2$ after Norrish (1954), who found that the swelling curve of montmorillonite extrapolated to $d = 21\text{\AA}$ for infinite concentration ($C^{-1/2} = 0$). The present results confirm this behavior,

the curves for pretreated montmorillonites and for vermiculite (Fig. 9) extrapolating to about 21\AA . This implies that a dead volume of 21\AA is associated with each silicate sheet and, since about 10\AA of this is the thickness of the montmorillonite sheet, there must be water films of $5-6\text{\AA}$, on either side of each sheet, not occupied by the ions of the diffuse layer. There is evidence that an organized water network exists on the clay surfaces, and this might be effectively "solid". In addition, Na^+ or Li^+ ions will move in solution with a hydration shell, and this could easily limit the distances of approach to the surface to $5-6\text{\AA}$.

Van der Waals' Attraction

Following Verwey and Overbeek (1948, p. 101), Norrish (1954) used, for the attraction between montmorillonite sheets, the expression

$$f = \{D^{-3} + (D + \delta)^{-3} - 2(D + \delta/2)^{-3}\} A/24\pi$$

where f is the attractive force per unit area

D is half distance between sheets, or $(d - 10)/2$

δ is the sheet thickness (10\AA)

and A is a constant, taken as 10^{-12} erg.

The validity of this formula has been questioned (Derjaguin *et al.*, 1954) and it seems now established (Black *et al.*, 1960) that for plate separations greater than 1000\AA , attraction should be proportional to the inverse fourth power of distance, with a constant of proportionality of $1-2 \times 10^{-19}$ erg cm. This is because electromagnetic retardation, not considered in the derivation of the above formula, has to be taken into account at sufficiently large distances (Casimir and Polder, 1948). However, there is evidence (Howe, Benton and Puddington, 1955; Overbeek and Sparnaay, 1954) that the above formula may be valid for separations smaller than 400\AA , but, if the forces calculated from it are in error, it is very probable that they will overestimate the attraction.

In Fig. 11 is plotted the calculated double layer repulsion between clay platelets, as a function of their separation, for several electrolyte concentrations. The calculated Van der Waals' force, from the above equation, is also shown. If the observed interlayer spacings were the result of a balance between these forces, the equilibrium positions would be at those values of D' where the curves intersect. The observed interlayer spacings are marked, and it is seen that, while the agreement is tolerable for small separations (stronger solutions), it is very poor for larger spacings (more dilute solutions). The curves for the double layer repulsion have been calculated on the basis of weak interaction. A fuller treatment would make very little difference in the regions where the agreement is poor. Likewise, any reasonable alteration of the value of A , for the Van der Waals' force, would not eliminate the disagreement.

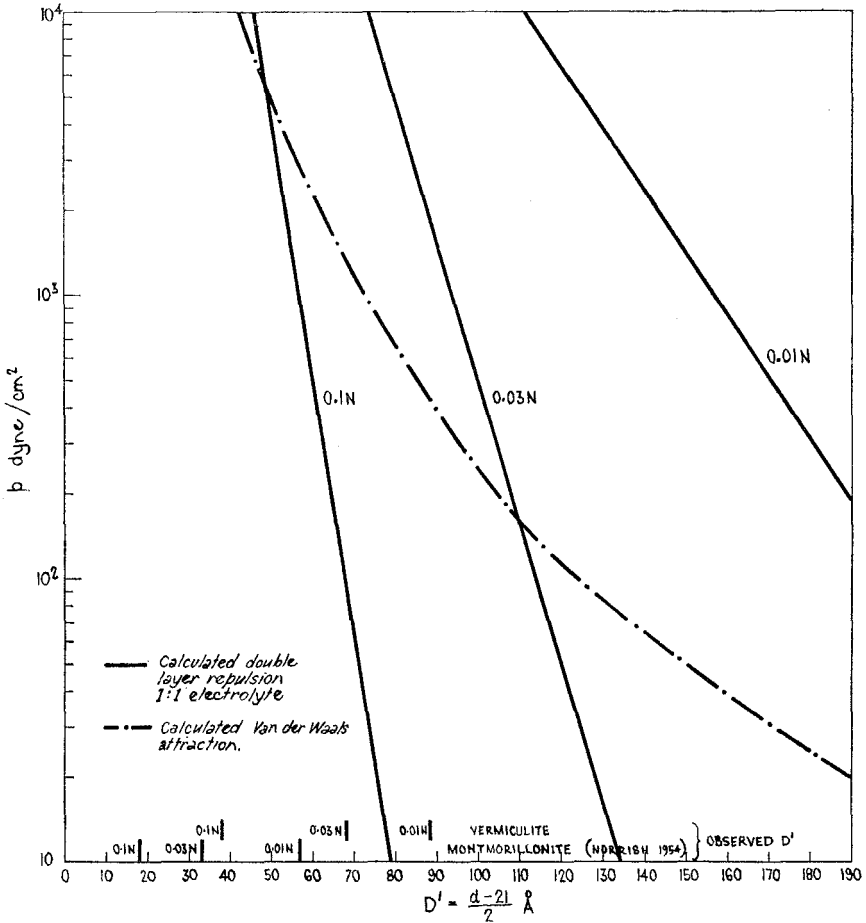


FIGURE 11.—Comparison between theoretical equilibrium distances and experimental spacings for montmorillonite and vermiculite.

That Van der Waals' attraction is inadequate is found from another consideration. Figure 12 shows the potential resulting from Van der Waals' attraction as a function of interlayer separation, and also shown is the thermal energy of montmorillonite sheets (2000 Å diameter). It is obvious that for film thicknesses of 70 Å or more, the trough produced in a total potential curve by Van der Waals' attraction would be too small to hold the sheets together. The calculated total potential curve for montmorillonite in 0.05 N NaCl is shown in Fig. 13, and it is seen that the trough is less than the thermal energy available to a sheet 2000 Å in diameter.

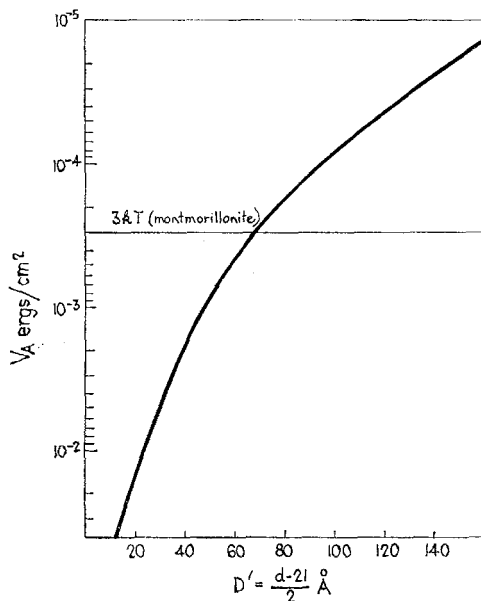


FIGURE 12.—Van der Waals' attractive potential between montmorillonite sheets.

Swelling of Li-vermiculite

Figure 6 shows that for Li-vermiculite there is very good agreement between observed and calculated swelling pressures at different water film thicknesses, and this confirms the earlier conclusion as to the validity of the diffuse double layer equations. This agreement makes it possible to place confidence in the repulsive forces calculated from the experimental data on

TABLE 3.—CALCULATED FORCES BETWEEN THE SHEETS OF VERMICULITE

C	$D' \times 10^8 \text{ cm}$	$p \times 10^{-4} \text{ dyn/cm}^2$	Extrapolation of pressure curve. Pressure $\times 10^{-4} \text{ dyn/cm}^2$
0.15	32	2.9	—
0.10	38	3.5	—
0.05	53	2.3	—
0.03	66	2.0	—
0.02	76	2.1	—
0.01	89	2.7	—
0.007	94	2.8	—
0.005	99	4.5	—
0.03	66	—	2.2
0.0	~ 115	—	2

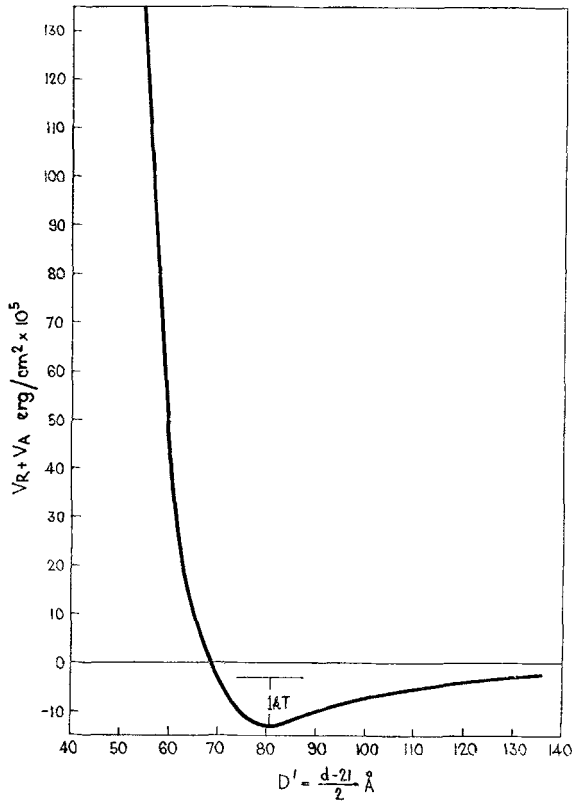


FIGURE 13.—Total potential curve for montmorillonite in 0.05N NaCl.

the swelling in LiCl solutions. Table 3 shows the rather surprising results of these calculations. For all concentrations the value of the repulsive force at the observed spacings appears to be constant at $\sim 2.5 \times 10^4$ dyn/cm². If the interlayer separations are the result of an equilibrium between opposing forces (this being indicated by the reversibility of the swelling) then the attractive forces must be of the same magnitude and have the same lack of dependence on distance and electrolyte concentration. Extrapolation of the curve of Fig. 6 to the spacing obtained under zero pressure (no applied load) leads to an empirical measurement of the internal load (attractive force). It is seen that this estimate, which is obtained independently of diffuse double layer theory, is in good agreement with the above calculations. Extrapolation of a swelling curve, similar to Fig. 6 but obtained with water as swelling medium, gives a similar value.

No suggestions are offered as to the origin of a force which could behave in the required manner. The force of gravity, which has the required independence of concentration and sheet separation, is, for the very thin samples used, several orders of magnitude too small.

Vermiculite commences swelling at a lower electrolyte concentration than montmorillonite (0.15N compared to $\sim 0.4N$). Qualitatively this behavior is what would be expected from its higher surface density of charge. At small separations (5 Å) the electrostatic attraction between sheets will be greater than for montmorillonite (Norrish, 1954). This limits the crystalline swelling to 15 Å, compared to 21 Å for Na-montmorillonite, and delays "explosion" to a gel until the external osmotic pressure of the electrolyte is less. Once swelling begins, vermiculite differs little from (Calgon) montmorillonite, but because of the above delay, the increase in interlayer spacing, from 15 Å to 82 Å, is much greater than that for montmorillonite, ~ 20 to 40 Å. These considerations suggest that, as the surface density of charge increases, the jump in spacing in passing from the crystalline to the gel state will become progressively larger. A limit to this behavior is set by the trend for swelling to begin at lower electrolyte concentrations, so that Li-vermiculites, of somewhat higher surface density of charge than that used, do not swell even in water.

The similarity of the d versus $C^{-1/2}$ curves of montmorillonite and vermiculite is shown by the fact that, although the lowest attainable gel spacing under no load is 82 Å for vermiculite, it can be reduced by an external load to ~ 50 Å (Fig. 6) and this does not differ greatly from the minimum of ~ 40 Å for montmorillonite.

The Swelling of Montmorillonite

Despite similarities, there are important differences in the swelling of vermiculite and montmorillonite. While the swelling of vermiculite appears to be reversible, both with respect to electrolyte concentration and applied pressure, montmorillonite, under identical conditions, swells less and shows hysteresis. The three decompression-compression cycles of Fig. 9 show clearly this behavior. Also, Rausell-Colom (1958) observed that when swollen montmorillonite flakes were put into progressively stronger NaCl solutions, no reduction in d (or in total volume of the flake) could be detected until the concentration reached $\sim 0.4N$, and then d dropped to 21 Å. Another important difference is that, in montmorillonite, swelling depends very strongly on pH or chemical treatment.

Although structurally similar, the montmorillonite and vermiculite used here differ in surface density of charge and, above all, in particle size. Since the double layer theory predicts that the difference in charge density will have little effect on the magnitude of the repulsive force, it appears that particle size causes the observed differences in swelling.

The concept of edge-to-face bonds resisting swelling (Rausell-Colom, 1958) is successful in explaining most of the observed features of the swelling of montmorillonite. Figure 14 shows the probable structure of a swollen oriented flake, with edge-to-face contacts between the elementary sheets in positions marked.

As swelling takes place sheets will move relative to one another by some bonds sliding on the surfaces without being broken, other bonds will be broken

and new ones will be made, with the result that, for any particular gel volume, the bonds will cause the structure to oppose change, either swelling or contraction. This explains the irreversibility of the swelling in salt solutions, and predicts that under load the swelling pressure for any film thickness should depend on the direction and distance from which it is approached, as observed.

The work of Schofield and Samson (1954), Nash (1960) and particularly van Olphen (1951) shows that bonds between sheets arise from the different charges carried by the faces (negative) and the edges (positive) at normal

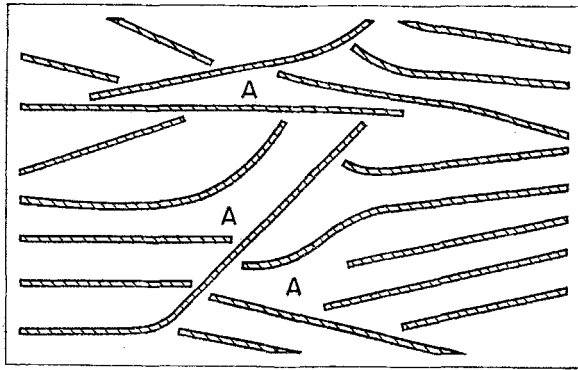


FIGURE 14.—Schematic representation of a swollen oriented aggregate of Na-montmorillonite. A, edge-to-face bonds.

pH, and that the charge carried by the edges can be reduced or reversed by increasing the pH or by treatment with complex anions, such as polymetaphosphate (Calgon). It is obvious that, as edges lose their charge, the effects of edge-to-face bonding will be reduced, i.e. swelling will increase. This explains why the Calgon-treated montmorillonite, which would be expected to have very few bonds (van Olphen, 1950), shows the greatest swelling, being comparable to that of vermiculite, where the effects of bonding are negligible or absent owing to its much larger sheets. The fact that two samples of montmorillonite, having different pretreatments but the same final pH, swelled differently suggests that, apart from control of the edge charge by pH, it is possible to remove permanently the sites of positive charge (Al³⁺) by appropriate treatment.

That edge-to-face bonds have the same effect as an applied load can be seen from a comparison of the diffraction from the acid- and Calgon-treated samples. For instance, Fig. 9 shows that the acid-treated montmorillonite swells in 0.05N NaCl to $D' = 23 \text{ \AA}$, and that under the same conditions, Calgon-treated montmorillonite has $D' = 48 \text{ \AA}$. But when the latter is made to swell against a load of $7 \times 10^5 \text{ dyn/cm}^2$ the swelling is limited to $D' = 23 \text{ \AA}$ (Fig. 10) and at the same time its diffraction pattern sharpens to be compar-

able to that of the acid-treated sample. This load is near to the repulsive pressure calculated from double layer theory for $C = 0.05 \text{ N}$ at $D' = 23 \text{ \AA}$, which suggests that the swelling of the acid-treated sample is limited by a considerable "internal" load and not by some chemical change affecting the diffuse double layer, e.g. Al ions fixed in the exchangeable positions on the montmorillonite surfaces.¹

When no load is applied to the specimen, the experimental D' obtained for a given concentration of electrolyte must represent the position at which the repulsion due to double layer interaction is balanced by the resistance arising from edge-to-face bonds. The variation of this resistive force with D' can thus be calculated, and it is found to range from about $2 \times 10^6 \text{ dyn/cm}^2$ for the acid-treated sample with a film thickness of $D' = 9 \text{ \AA}$ ($C = 0.3 \text{ N}$), to 10^4 dyn/cm^2 for the Calgon-treated sample with a film thickness of $D' = 106 \text{ \AA}$ ($C = 0.01 \text{ N}$). The decrease of the force with D' will be due to bonds being broken as the gel volume increases.

The difference in the swelling pressures given by the decompression and compression curves of Fig. 10 at a particular film thickness can also be used to obtain an idea of the magnitude of the resistive force and of its variation with D' . It is seen that this ranges from $\sim 6 \times 10^5 \text{ dyn/cm}^2$ to $\sim 6 \times 10^4 \text{ dyn/cm}^2$ as D' goes from 18 \AA to 45 \AA .

From measurements of the yield stress of gels van Olphen (1956) determined the force of a single edge-to-face bond as $\sim 10^{-4} \text{ dyn}$. Rausell-Colom (1958) calculated the electrostatic attraction between the negative surface of a montmorillonite sheet and each charge of $+e$, on an edge in contact with it, as $\sim 7 \times 10^{-5} \text{ dyn}$. The above estimates are in substantial agreement, and imply that a number of bonds, ranging from 2×10^{10} per cm^2 to 10^8 per cm^2 (i.e. for sheets of 2000 \AA diameter, 8 to 0.04 bonds per sheet), would be sufficient to create resistive forces of the magnitude required.

With no external load, swelling is opposed only by these frictional forces, and it is easy to see that, depending on many fortuitous circumstances, different sheets will move farther apart than others, i.e. very diffuse and asymmetrical distributions of interlayer distances can result, as observed. The application of an external load will reduce the fortuitously large spacings, and so sharpen the distribution before the mode is affected. Reducing the double layer repulsion with stronger concentrations of electrolyte will have little effect on a previously swollen specimen, since, although the tendency to swell is removed, there is no effective force to bring the sheets together against the resistance of the bonds (Van der Waals' attraction being much smaller in magnitude). As mentioned earlier, Rausell-Colom (1958) observed that the sheets did not come together (to $d = 21 \text{ \AA}$) until the concentration reached $\sim 0.4 \text{ N}$. Similarly, Hight (1962), studying the effect of salt additions to montmorillonite suspensions, could not detect the presence of any interlayer spacing until, when the concentration reached 0.4 N , a spacing of $d = 19 \text{ \AA}$ was observed. At $d = 20 \text{ \AA}$ diffuse double layers do not exist, so that

¹ The treatment at low pH in the presence of a strong NaCl solution is one designed to remove exchangeable (Al Aldrich and Buchanan, 1958).

the above spacings are not due to any reduction in the thickness of the diffuse double layer, but to its destruction. These results suggest that, where flocculation occurs in a concentration of less than 0.4N NaCl, it is due to edge-to-face interaction rather than to interaction between diffuse double layers of parallel sheets. This conclusion is supported by the observation that, with an optimum amount of Calgon added (very few edge-to-face bonds), Na-montmorillonite sols do not flocculate until the NaCl concentration reaches 0.4N (van Olphen, 1950).

CONCLUSIONS

The present results confirm that double layer repulsive forces cause the swelling of Na-montmorillonite and Li-vermiculite, and that the magnitude of van der Waals' attraction at the observed interlayer distances is insufficient to balance this repulsion.

In montmorillonite, edge-to-face bonds provide a resistance which limits the swelling of the clay. In magnitude this resistive force, and therefore swelling, depends on chemical treatment. The resistance opposes both expansion and contraction of the gel structure, giving rise to a marked hysteresis in the swelling.

In vermiculite crystals, because the sheets are considerably larger, the force arising from edge-to-face bonds appears to be small or absent. Swelling is therefore greater than in montmorillonite, and is reversible. Calculations show that the force limiting swelling is more or less independent of sheet separation and electrolyte concentration, and its magnitude is $\sim 2.5 \times 10^4$ dyn/cm².

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