DIRECT MEASUREMENT OF THE RELATION BETWEEN SWELLING PRESSURE AND INTERLAYER DISTANCE IN Li-VERMICULITE[1]

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Abstract—To test the double-layer theory of swelling as applied to layer silicates, the interlayer separation, λ, in a Li-saturated vermiculite from Grouse Creek, Utah, was measured as a function of the swelling pressure, Π. An oriented sample of the vermiculite (46–105 μm) was placed in an environmental chamber mounted on an X-ray diffractometer and compressed between N_2 gas and a porous membrane in contact with a solution draining to the outside atmosphere. After equilibration at each of several successively higher gas pressures, the c-axis spacing was measured by X-ray diffraction, and the corresponding λ was calculated by subtracting the thickness of an elementary silicate layer. The results of these measurements showed that: (1) the relation between Π and λ for vermiculite is the same as that previously observed for Na-montmorillonite, i.e., Π is an exponential function of $1/\lambda$; (2) the values of Π predicted by double-layer theory are much smaller than those observed if the surface potential is assigned the appropriate value; and (3) the observed relation between Π and λ does not have the form predicted by this theory. On the basis of these results, a repulsive force not ascribable to double-layer overlap must be primarily responsible for swelling; this force must result from the in-depth perturbation of the water by the surfaces of the vermiculite layers.

Key Words—Double-layer theory, Interlayer distance, Swelling pressure, Vermiculite, X-ray diffraction.

INTRODUCTION

The swelling of clays and other layer silicates is a phenomenon of great importance in nature. It affects the drainage of soils, the hydrology of geological formations, the stability of building foundations, etc. The general view is that swelling is due to excess osmotic pressure in the solution between the superimposed silicate layers and that it can be described by double-layer theory (Schofield, 1946; Norrish, 1954; Bolt and Miller, 1955; Warkentin *et al.*, 1957; Norrish and Rausell-Colom, 1963; van Olphen, 1963; Quirk, 1968). A second view, which has been held primarily by Low and his coworkers (Low and Deming, 1953; Hemwall and Low, 1956; Ravina and Low, 1972; Low and Margheim, 1979; Low, 1980, 1981; Viani *et al.*, 1983) and by Derjaguin and his coworkers (Derjaguin *et al.*, 1954; Derjaguin and Churaev, 1974) is that surface hydration also contributes to the swelling of clays and other colloids. The latter view has been advanced recently by Israelachvili and Adams (1978) and Pashley (1981a, 1981b).

To test rigorously the adequacy of double-layer theory, the repulsive force of the silicate layers must be determined directly and accurately as a function of the distance between them under conditions that allow the surface charge density of the layers and the electrolyte concentration of the external solution to be assessed. To the authors' knowledge, only Norrish and Rausell-

Colom (1963), Israelachvili and Adams (1978), Pashley (1981a, 1981b), and Viani *et al.* (1983) have attempted such a determination. Norrish and Rausell-Colom studied montmorillonite and vermiculite, Israelachvili and Adams and Pashley studied muscovite mica, and Viani *et al.* studied montmorillonite. The results for muscovite mica and montmorillonite are in good agreement (Pashley and Quirk, 1983; Viani *et al.*, 1983). Except for Norrish and Rausell-Colom (1963), all of these investigators concluded that hydration forces were operative.

Vermiculite is an excellent mineral with which to investigate the applicability of double-layer theory. In keeping with the requirements of the theory, it has planar parallel layers that have a relatively high surface-charge density and are sufficiently extensive for "edge effects" to be insignificant. Moreover, the three-dimensional order of vermiculite crystals enhances the possibility of obtaining reliable interlayer distances by X-ray diffraction. The objective of the present work, therefore, was to confirm earlier results with montmorillonite (Viani *et al.*, 1983) by performing similar experiments with vermiculite. In this regard, it should be noted that the results of Norrish and Rausell-Colom (1963) were not suitable for the present purpose because they used a different method of establishing the interlayer force, their X-ray technique was less precise (because of low intensities and visual estimation of peak positions) and, hence, yielded less reliable interlayer distances, and their samples were equilibrated with a solution having a different electrolyte concentration.
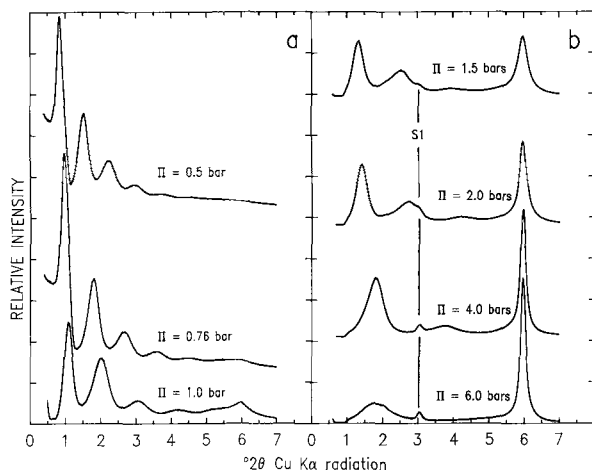

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Figure 1. X-ray diffraction patterns of Utah Li-vermiculite in equilibrium with a 10^{-4} N LiCl solution at seven applied pressures (each division on the ordinate axis corresponds to 2400 count/sec in (a) and to 4800 count/sec in (b)).
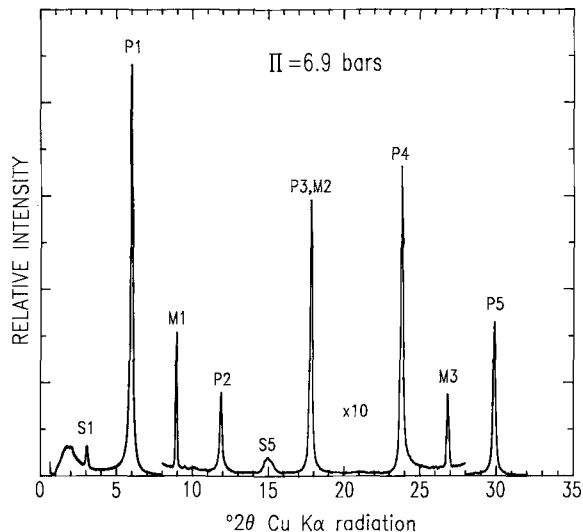

Figure 2. X-ray diffraction patterns of Utah Li-vermiculite in equilibrium with a 10^{-4} N LiCl solution at an applied pressure of 6.9 bar (each division on the ordinate axis corresponds to 5000 count/sec; between 8 and 28°2θ the relative intensity is multiplied by a factor of 10).

MATERIALS AND METHODS

Specimens of vermiculite having a relatively low surface charge density will expand in dilute aqueous solutions beyond a c-axis spacing of 14–15 Å if the exchange sites are saturated with Li (Walker, 1960; Norrish and Rausell-Colom, 1963). The Li-vermiculite used in the present experiments was prepared from the 46–105-μm fraction of the Na-saturated Grouse Creek, Utah, vermiculite studied by Roth et al. (1969). About 0.7 g of the Na-vermiculite was treated to remove free iron oxides by the method of Jackson (1974). The sample was then treated for 1 hr at 90°C with a mixture containing one part 30% H_2O_2 and four parts 1 N Na-acetate (pH 5) to reoxidize the octahedral iron in the vermiculite. Subsequently, to replace the Na^+ by Li^+, the vermiculite was washed once with 1 N LiCl and then suspended in 1 N LiCl at 60°C for 2 months. During this period, the LiCl solution was replaced seven times. The vermiculite was then washed once with distilled water and five times with a 10^{-4} N LiCl solution before being suspended at a concentration of ~10 mg/ml in the latter solution.

The method of Viani et al. (1983) was used to determine the relation between the swelling pressure, Π, and c-axis spacing of Li-vermiculite in equilibrium with a 10^{-4} N LiCl solution. Briefly, an oriented sample of the clay was placed in an environmental chamber mounted on an X-ray diffractometer and then compressed between N_2 gas and a porous membrane in contact with a solution that drains to the outside atmosphere. After equilibration at each of several successively higher gas pressures, the c-axis spacing was measured. It should be noted that, at equilibrium, Π equals the applied gas pressure. Also, the interlayer

distance, λ, was obtained by subtracting the thickness of the silicate layers (9.3 Å) from the c-axis spacing.

RESULTS AND DISCUSSION

Figure 1 shows examples of the smoothed X-ray diffraction patterns (not corrected for Lp effects) between 0.5° and 8°2θ of the Utah Li-vermiculite at seven values of Π. Although they are not all evident in the figure, as many as five or six higher-order diffraction peaks were revealed, especially at low values of Π, by scale expansion. Figure 2 shows one example of the diffraction patterns for the range 0.5° to 32°2θ. In these examples, all the peaks except those labeled P, S, and M are 00l reflections from the fully expanded layers. The peaks labeled P are 00l reflections from the partially expanded (~15 Å) layers, the peaks labeled S represent 00l reflections from the layers in a 29-Å (14.5 + 14.5 Å) superlattice, and the peaks labeled M represent 00l reflections from the internal standard (mica). All diffraction peaks in both figures are well defined and readily yielded accurate values of the corresponding c-axis spacings.

Note from Figure 1 that the partially expanded phase developed progressively from the expanded phase as Π increased, a transformation that was also observed for certain Na-montmorillonites (Viani et al., 1983). The coexistence of partially expanded and fully expanded phases has been observed by others (Norrish, 1954; Foster et al., 1955; Norrish and Rausell-Colom, 1963; Fink and Thomas, 1964; Rhoades et al., 1969) under a variety of experimental conditions and is, apparently, a general feature of many silicate-water sys-
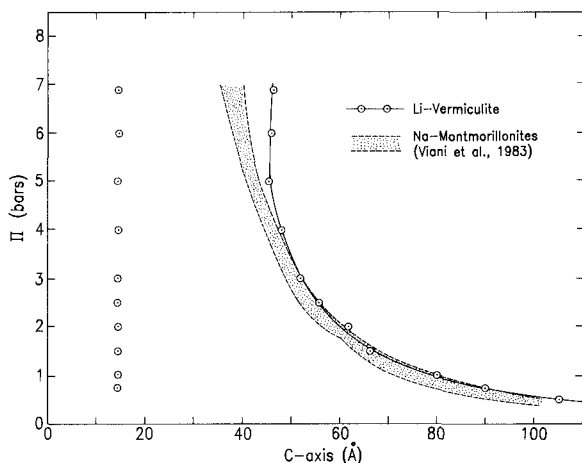
Figure 3. Comparison of the relations between Π and c-axis spacing for the expanded phases of Utah Li-vermiculite and various Na-montmorillonites in equilibrium with 10^{-4} N chloride solutions of the respective cations. (Note the existence of a partially expanded phase at 15 Å.)

tems. The superlattice phase was first evident at $\Pi = 1.5$ bar, but, in contrast with the partially expanded phase, it showed no apparent development with increasing Π. The c-axis spacings of the partially expanded phase and superlattice phase were independent of Π. On the other hand, the diffraction peaks of the fully expanded phase shifted progressively to higher values of 2θ (smaller c-axis spacings) with increasing Π. In the present paper, attention is focused on the fully expanded layers because they are the only ones for which the relation between *interlayer force* and *interlayer distance* can be determined.

X-ray diffraction patterns in which the higher basal orders are differentially broadened and reduced in intensity (or completely absent), such as those for the fully expanded layers in Figure 1, indicate a structure in which the c-axis spacings of the elementary silicate layers are distributed about a modal value (Norrish, 1954; Norrish and Rausell-Colom, 1963; Cebula *et al.*, 1979). The breadth of the distribution is directly related to the number and width of the 00*l* peaks (Guinier, 1963, 295–309). Therefore, it is evident that the distribution of the c-axis spacings of the fully expanded layers is quite narrow.

It is apparent from Figure 1 that, as Π increased, the 00*l* peaks of the fully expanded layers became broader and the number of observable higher orders decreased. This observation does not necessarily mean that there was an increase in the breadth of the distribution of c-axis spacings about the mode or a decrease in the size of the diffracting domain, because, for a given distribution and domain size, the width of any particular basal reflection varies inversely with c-axis spacing

(Guinier, 1963). It is reasonable to postulate, however, that some of the observed broadening resulted from a reduction in the domain size of the fully expanded layers due to the progressive increase in the fraction of partially expanded layers throughout the sample.

Figure 3 compares the results obtained for the Utah Li-vermiculite with those obtained by Viani *et al.* (1983) for seven different montmorillonites. In this illustration, the lines defining the upper and lower limits of the stippled area coincide with extreme portions of the collective curves of Π vs. c-axis spacing for the montmorillonites. In other words, all of the curves for the montmorillonites fall within the stippled area. Therefore, it is evident that, except when $\Pi > 5.0$ bar, the relation between Π and c-axis spacing is essentially the same for the fully expanded layers of the two minerals. Viani *et al.* (1983) showed, by the same kind of comparison, that their data for the Na-montmorillonites agreed with the data of Pashley (1981b) for Na-saturated muscovite. Therefore, the location and magnitude of charge, lateral dimensions, etc., of the silicate layers must not affect significantly the swelling of fully expanded phases. On the other hand, double-layer theory predicts that swelling depends on the magnitude of the charge.

To emphasize that the data for Li-vermiculite agree with those for Na-montmorillonite, the diffraction patterns (not corrected for Lp effects) of the two minerals at an arbitrarily chosen Π (1.5 bar) are shown in Figure 4. Although the 00*l* peaks of the Li-vermiculite are narrower and more intense than those for the Na-montmorillonite, their c-axis spacings (after Lp correction) are almost exactly the same. Note that, for the montmorillonite, precise c-axis spacings are also readily obtainable.

Figure 3 shows that the c-axis spacing of the expanded layers of Li-vermiculite remained virtually constant after Π exceeded ~5.0 bar. As shown in Figure 1, however, the proportion of these layers continued to decrease as more of them jumped to a fixed c-axis spacing of ~15 Å, i.e., as more of them became partially expanded. These observations are indicative of an energy barrier which became very steep near its summit and which had to be surmounted by the expanded layers before they fell into the primary energy minimum on the opposite side. Although conventional theory (e.g., Verwey and Overbeek, 1948; van Olphen, 1963) predicts that summing the double-layer repulsive energy and the van der Waals attractive energy yields two energy minima separated by an energy barrier, the predicted barrier is never so steep that λ (or the c-axis spacing) remains constant with increasing Π. Therefore, we conclude that double-layer repulsion cannot explain the results for the Li-vermiculite. An additional repulsive force must be active. We suggest that this force is the hydration force arising from the

overlapping of the hydration shells of adjacent layers and that the structural integrity of these shells increases suddenly when the c-axis spacing is ~45 Å.

Pashley (1981b, 1982) postulated that the cooperative hydration of Stern-layer cations is responsible for the additional repulsive force that has been found between mica sheets at small separations (e.g., Pashley, 1982; Pashley and Quirk, 1983). We doubt this postulate because it is not consistent with our observation that, when $\Pi \leq 5.0$ bar, the relation between interlayer force and interlayer distance was essentially the same for vermiculite, montmorillonite, and mica despite the fact that these minerals were not all saturated with the same cation and had widely different surface charge densities (and, hence, numbers of exchangeable cations per unit area). As has been stated elsewhere (e.g., Low and Margheim, 1979; Low, 1980; Viani et al., 1983), the repulsive force between clay layers must arise from the non-specific interaction of the water with the surfaces of these layers. It is conceivable, however, that the cooperative hydration of the Stern-layer cations does contribute substantially to the integrity of the water structure in a relatively shallow zone near the mineral surface and that this contribution is reflected in the constancy of the c-axis spacing when $\Pi > 5.0$ bar.

Conventional electric double-layer theory is applicable to the diffuse layer only, and so the boundary values used in solving the relevant equations must be those at the inner boundary of this layer. In the past, it has been assumed that the inner boundary of the diffuse layer coincides with the silicate surface and that the diffuse-layer charge arises from ionic substitution. Accordingly, it has been assumed that the surface charge density is constant and equals the quotient of the cation-exchange capacity and surface area. From the results of Low (1981) and Chan et al. (1984), however, and from unpublished results obtained recently in this laboratory, it appears that: (1) most of the exchangeable cations are adsorbed on the silicate surface in a Stern layer, (2) the values of σ_δ, the charge density at the inner boundary of the diffuse layer, and of ψ_δ, the potential at this boundary, are much smaller than the corresponding values at the silicate surface, (3) ψ_δ is constant but σ_δ is variable, and (4) the electrophoretically measured ζ potential provides a good estimate of ψ_δ. The ζ potential of Li-vermiculite in 10^{-4} N LiCl is between 50 and 90 mV (Friend and Hunter, 1970). Its precise value depends on the corrections that are appropriate. Therefore, it is reasonable to assume that the ψ_δ for Li-vermiculite is constant and within the limits of 50 and 90 mV.

Figure 5 compares the observed relation between Π and λ with the theoretical relations for different constant values of ψ_δ. The theoretical relations were determined by substituting these values of ψ_δ for the surface potential, ψ_0, in the equations used by Viani et al.
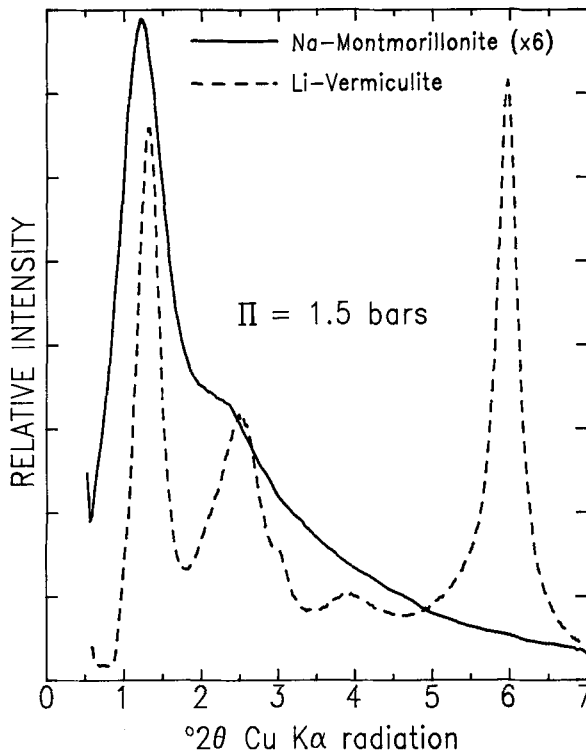

Figure 4. X-ray diffraction patterns of Utah Li-vermiculite and Upton Na-montmorillonite in equilibrium with a 10^{-4} N LiCl and a 10^{-4} N NaCl solution, respectively, at an applied pressure of 1.5 bar (each division on the ordinate axis corresponds to 1000 count/sec).

(1983) and allowing ψ_d, the potential at the midplane, to vary with d, the distance between this plane and the inner boundary of the diffuse layer. In addition, δ, the thickness of the Stern layer, was assumed to be 5.0 Å in the relation $d = (\lambda - 2\delta)/2$. Note from this figure that none of the theoretical curves coincides with, or even approximates, the observed curve. Also note that, if ψ_δ lies within the afore-mentioned limits, the theoretical value of Π at any value of λ is insignificant compared to the observed value.

The relation between Π and λ for Na-montmorillonites has been shown previously (Viani et al., 1983) to be

$$(\Pi + 1) = \exp k[(1/\lambda) - (1/\lambda^0)] = b \exp k(1/\lambda) \quad (1)$$

or

$$\ln(\Pi + 1) = k(1/\lambda) + \ln b, \quad (2)$$

where k is a constant, $b = \exp[-k/\lambda^0]$, and λ^0 is the interlayer separation when $\Pi = 0$. As shown in Figure 6, this relationship holds also for Li-vermiculite until the relatively steep region of the energy barrier is encountered at $1/\lambda = 0.028$ Å^{-1} ($\lambda = 35$ Å).
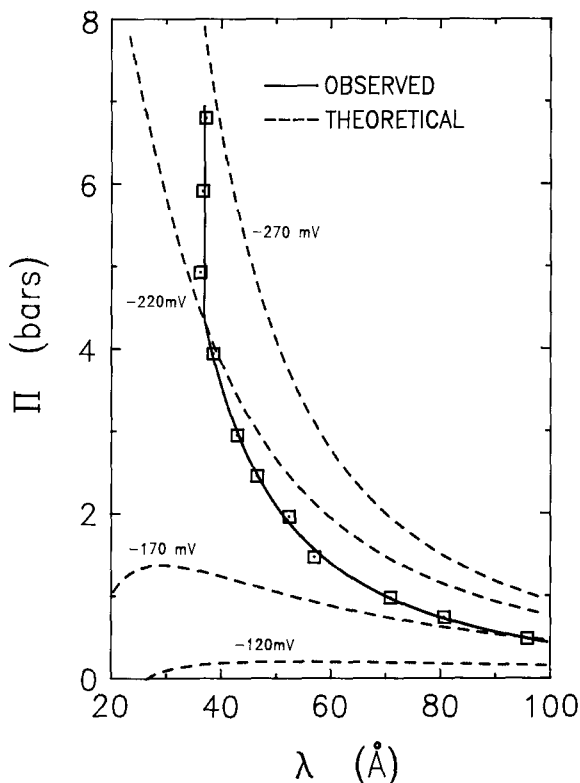
Figure 5. Comparison of the observed relation between Π and λ for Utah Li-vermiculite with the theoretical relations for different constant values of ψ_δ.
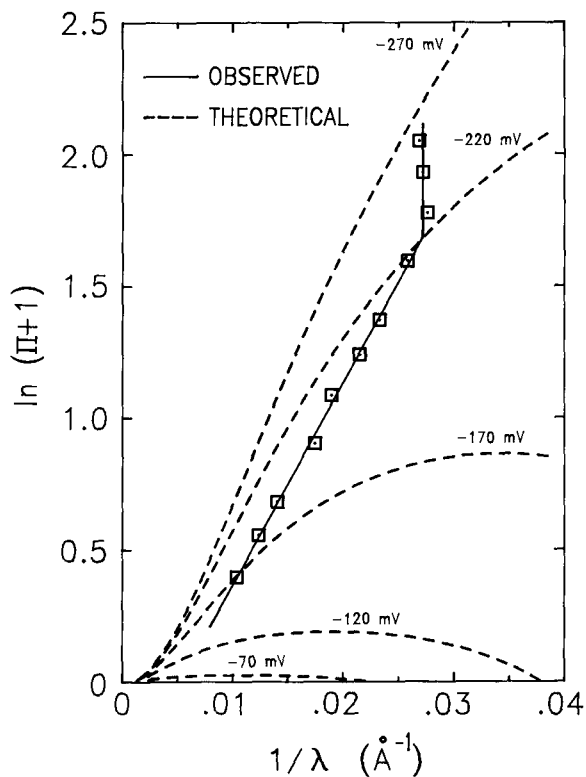

Figure 6. Comparison of the observed relation between $\ln(\Pi + 1)$ and $1/\lambda$ for Utah Li-vermiculite with the theoretical relations for different constant values of ψ_δ.

To emphasize that the theoretical relations between Π and λ do not have the *form* of the observed relation as expressed by Eq. (1), the respective theoretical plots of $\ln(\Pi + 1)$ vs. $1/\lambda$ are also included in Figure 6. Obviously these plots are curvilinear at all values of ψ_δ. The same was true when σ_δ was held constant (Viani *et al.*, 1983). Therefore, the inability of double-layer theory to predict the linear relation between $\ln(\Pi + 1)$ and $1/\lambda$ is independent of which parameter, ψ_δ or σ_δ, is held constant. Moreover, it is doubtful that the predicted relations can be linearized by modifying the theory to take into account such factors as the non-ideality of the interlayer solution, the volume occupied by the ions, or the finite volume of the external solution. Either the theory is fundamentally wrong or it is not applicable to clays because their diffuse layers are poorly developed and double-layer repulsion is not the primary cause of swelling. As mentioned above, we subscribe to the latter alternative.

In previous papers (e.g., Low, 1980; Viani *et al.*, 1983) empirical equations describing the swelling of clay-water systems and the properties of the water within these systems were combined to yield

$$(\Pi + 1) = B(J_i/J_i^0)^{\alpha/\beta}, \qquad (3)$$

where J is the value of any property, i, of the water within the system, J^0 is the value of the same property for pure bulk water, and B, α, and β are constants. Eq. (3) shows that Π and J/J^0 are related and suggests that the development of Π is caused by the same factor that causes J to deviate from J^0. Because the present evidence indicates that diffuse ionic layers cannot account for the development of Π, and because earlier evidence (Mulla and Low, 1983; Sun, 1983) indicates that such layers cannot account for the deviation of J from J^0, both Π and J must be affected by interaction of the water with the surfaces of the silicate layers. Evidently, this interaction affects $\bar{G} - G^0$, the relative partial molar free energy, and other properties of the interlayer water and causes the development of Π in keeping with the thermodynamic equation

$$\bar{G} - G^0 = -\bar{v}\Pi, \qquad (4)$$

where $\bar{v}$ is the partial molar volume of the water. A derivation of Eq. (4) was given by Low and Anderson (1958).

It is apparent that the interlayer separation at which $\Pi = 0$ must be approximately twice the thickness of the water layer that is influenced by interaction with the surface. The constants in Eq. (1) (k = 77.3, ln

b = -0.400) were evaluated by linear regression of the data for values of $\Pi \leq 5$ bar and used to calculate the thickness ($\lambda_0/2$) of this layer. The resulting value, 97 Å, is slightly greater than the thickness of analogous layers (67–93 Å) developed on Na-montmorillonites (Viani et al., 1983). The value of the corresponding λ_0, 193 Å, agrees with the observation of Norrish and Rausell-Colom (1963) that the free swelling of Li-vermiculite (i.e., at $\Pi = 0$) tends toward a maximum interlayer separation of 220 Å as the concentration of salt in the external solution tends to zero.

In summary, when λ exceeds ~35 Å, the relation between Π and λ is essentially the same for the *expanded layers* of vermiculite as for the *expanded layers* of montmorillonite. The electric double-layer theory predicts neither the form of this relation nor its insensitivity to surface charge density. Evidently, the theory does not apply because the diffuse layers of clays are poorly developed and double-layer repulsion is not the primary cause of swelling. In view of the relation between Π and the properties of the interlayer water, it is concluded that the primary cause of swelling is interaction of the water with the surfaces of the silicate layers.

ACKNOWLEDGMENTS

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