SWELLING PRESSURE OF MONTMORILLONITE LAYERS VERSUS H-O-H BENDING FREQUENCY OF THE INTERLAYER WATER

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Abstract—The in-depth perturbation of vicinal water by the surfaces of montmorillonite layers was investigated by relating the swelling pressure, Π, of the montmorillonite layers to the H-O-H bending frequency, ν_2, of the interlayer water. For this purpose, an oriented montmorillonite gel was deposited on a porous filter in an environmental chamber. On its underside the filter was in contact with a solution maintained at atmospheric pressure. By admitting nitrogen gas at a known pressure to the environmental chamber, water was squeezed from the gel into the solution until equilibrium was reached and Π equalled the applied pressure. Then the gel was divided into 2 parts. One part was used for the gravimetric determination of the water content, m_w/m_c. It was possible, therefore, to determine m_w/m_c as a function of Π. The other part of the sample was transferred to an FTIR spectrometer where the ν_2 of the water within it was measured by attenuated total reflectance. Thus, the same samples were used to determine the dependence of both Π and ν_2 on m_w/m_c. It was found that Π and ν_2 were both exponential functions of m_c/m_w and so a linear relation was found between $\ln(\Pi + 1)$ and $\ln(\nu_2/\nu_2^\circ)$, where ν_2° is the H-O-H bending frequency of bulk water. These results strongly support the conclusion that the in-depth perturbation of the water by the surfaces of the montmorillonite layers is primarily responsible for both the development of Π and the departure of ν_2 from ν_2°.

Key Words—Bending Frequency, Hydration, Infrared Spectroscopy, Interlayer Force, Interlayer Water, Montmorillonite, Swelling Pressure.

INTRODUCTION

The swelling of clay is among the most important of the phenomena occurring in the earth's crust and, hence, has been the subject of many experiments (Norrish 1954; Barclay and Ottewill 1970; Callaghan and Ottewill 1975; Derjaguin and Churaev 1974; Lubetkin et al. 1984; Low 1979, 1980, 1987a; Israelachvili and Adams 1978). However, the cause of swelling is still debated. Low (1980) observed that the swelling (disjoining) pressure, Π, of a clay is related to the mass ratio of water to clay, m_w/m_c, by an empirical equation:

$$(\Pi + P_a)/P_a = B \exp\left(\frac{\alpha}{m_w/m_c}\right) = B \exp[\alpha(m_c/m_w)] \quad [1]$$

where P_a is the pressure of the atmosphere, $B = \exp[-\alpha/(m_w/m_c)^\circ]$, α is a constant that depends primarily on the magnitude of the surface area, S, of the clay, and $(m_w/m_c)^\circ$ is the value of m_w/m_c when $\Pi = 0$. When the pressure is expressed in atmospheres, this equation becomes:

$$(\Pi + 1) = B \exp\left(\frac{\alpha}{m_w/m_c}\right) = B \exp[\alpha(m_c/m_w)]. \quad [2]$$

An alternative form of Equation [2] relates Π to λ, the interlayer distance (Viani et al. 1983, 1985; Wu et al. 1989; Zhang et al. 1995). It is:

$$(\Pi + 1) = b \exp\left(\frac{k}{\lambda}\right) \quad [3]$$

where b and k are constants. Theoretical studies have supported this equation (Achanta et al. 1994; Achanta and Cushman 1994).

Several properties of water in montmorillonite-water systems have been studied in this laboratory (Anderson and Low 1958; Oster and Low 1964; Kay and Low 1975; Low 1976; Low 1979; Clementz and Low 1976; Sallé de Chou et al. 1980; Mulla and Low 1983; Sun et al. 1986; Low 1987a, 1987b; and Fu et al. 1990). The accumulated evidence has shown that the thermodynamic, hydrodynamic and spectroscopic properties of water in these systems differ from those of pure bulk water and are described by the equation:

$$J_i/J_i^\circ = \exp\left(\frac{\beta_i}{m_w/m_c}\right) = \exp[\beta_i(m_c/m_w)] \quad [4]$$

where J_i is the magnitude of any property, i, of the water in the montmorillonite-water system, J_i° is the magnitude of the same property for pure bulk water, and β_i is a constant. Note the similarity between Equations [2] and [4]. This similarity suggests that both Π and J_i depend on the same cause, namely, the perturbation of vicinal water (interlayer and intracrystalline water) by the surfaces of the clay particles (Low 1987a). Combination of these equations yields:

$$(\Pi + 1) = B (J_i/J_i^\circ)^{\alpha/\beta} \quad [5]$$

Low (1987b, 1992) has shown that Equation [5] applies to smectites when J is the molar absorptivity of interlayer water. Its validity for several soil clays has been established by Gan (1990) when J is the O-D stretching frequency of a clay suspension in 8% D_2O-
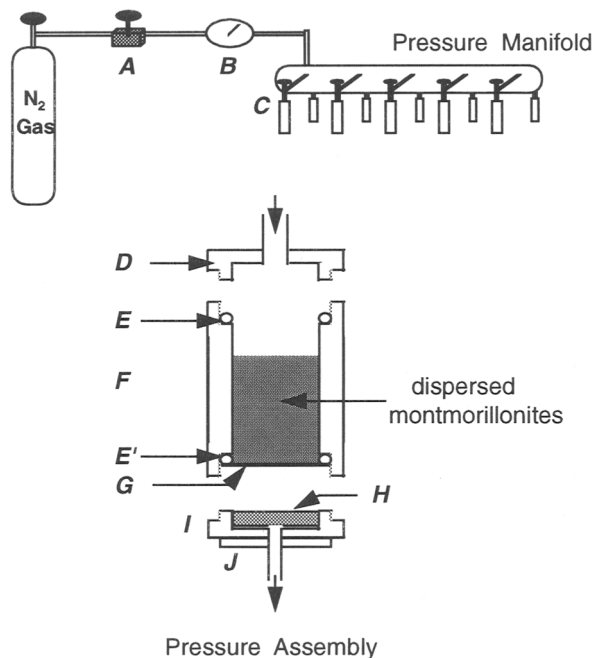
Figure 1. Schematic illustration of the apparatus for measuring the swelling pressure of clay-water samples.
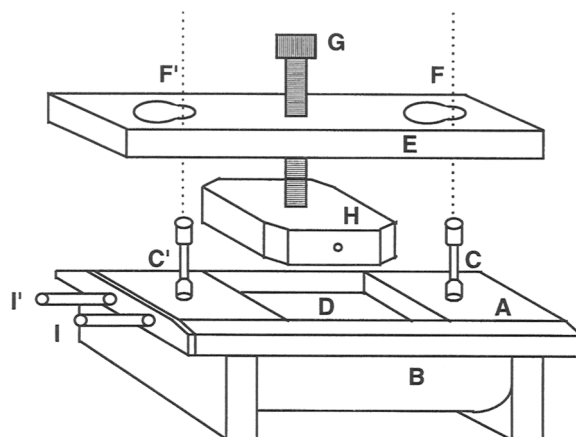

Figure 2. Schematic illustration of the sample cell of the ATR accessory.

steel barrel *(F)* having a capacity of 3.5 mL, a Millipore filter *(G)* with pores of 0.025 μm in diameter, a flat stainless-steel filter *(H)*, and a stainless-steel base *(I)*. In the flat, upper surface of the base (which sup-

92% H_2O. But in those studies Π and *J* were determined at different times on different samples. In the present study, we propose to demonstrate the validity of Equation [5] by using ν_2, the frequency of the H-O-H bending vibration, as the water property, and measuring both Π and ν_2 on the same samples.

MATERIALS AND METHODS

A freeze-dried, Na-saturated, <2-μm fraction of the montmorillonite from Upton, Wyoming, was prepared by a procedure described by Yan, Low and Roth (1996). Li-saturated montmorillonite was prepared from this Na-saturated montmorillonite by the same procedure. The Na- or Li-montmorillonite was mixed with deionized-distilled water to form a suspension containing 1% montmorillonite by weight. The suspension was allowed to equilibrate for 24–48 h before each measurement.

The apparatus for measuring the relation between Π and m_w/m_c is shown in Figure 1. This apparatus is similar to that used by Low (1980). It consisted of a N_2 gas tank connected through a Cartesian manostat *(A)* and a sensitive Heise pressure gauge *(B)* (Model H20664, Newtown, Connecticut) to a pressure manifold. Needle valves *(C)* served as outlets at 5 equidistant locations on both sides of the manifold. Each needle valve was connected by means of a Luer-lok fitting to the cap *(D)* of a stainless-steel pressure assembly. Besides the cap *(D)* the components of the pressure assembly were Viton rubber O-rings *(E* and *E′)* between separable sections, a Teflon-coated stainless-
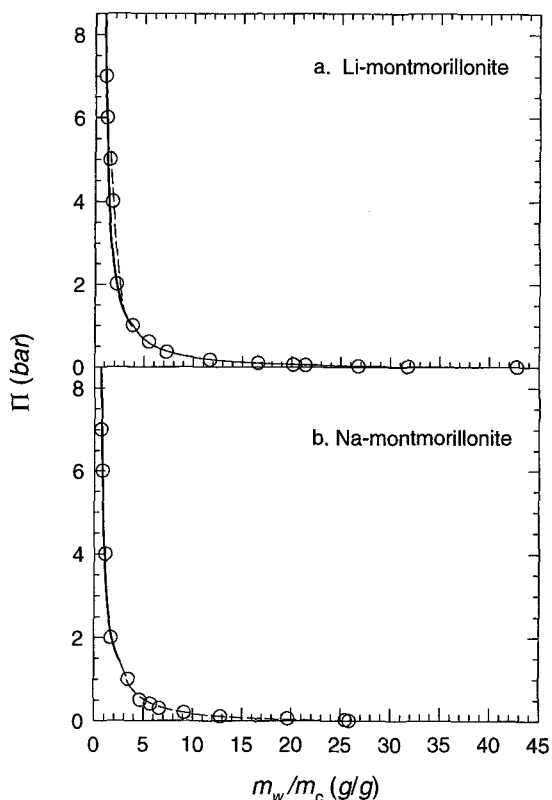

Figure 3. Relation between the swelling pressure, Π, and the mass ratio of water to clay, m_w/m_c, for (a) Li-montmorillonite, and (b) Na-montmorillonite. The dashed line is the range of higher water content and the solid line is the range of lower water content.
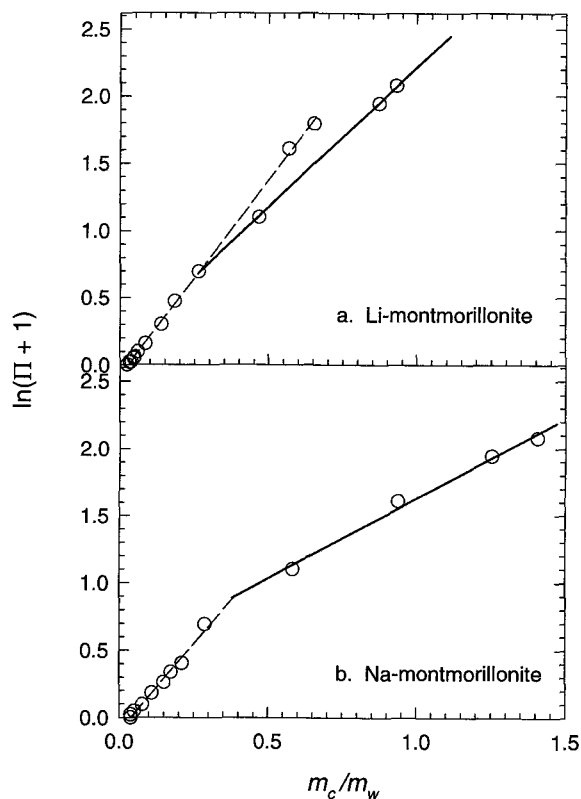
Figure 4.   Relation between the $\ln(\Pi + 1)$ and m_c/m_w for (a) Li-montmorillonite, and (b) Na-montmorillonite. The dashed line is the range of higher water content and the solid line is the range of lower water content.

Table 1.   Statistically determined parameters in Equation [2].

Clay		α	β	R^2†
Li-montmorillonite	—below break	2.9088	0.9229	1.00
	—above break	2.0762	1.1499	1.00
Na-montmorillonite	—below break	2.5857	0.9046	0.98
	—above break	1.1960	1.5405	0.99

† R is the correlation coefficient.

After reaching equilibrium, part of the sample was quickly removed from the pressure assembly and analyzed gravimetrically to determine its m_w/m_c. The other part was transferred to the sample cell shown in Figure 2. This cell was a component of a single pass, variable angle, attenuated total reflectance (ATR) accessory manufactured by Harrick Scientific Corporation, Ossining, New York. It consisted of 2 sections. The lower section was a flat plate (A) that had a ZnSe hemicylinder (B) attached to its underside, vertical rods with enlarged heads (C and C') extending from its upper surface and a central recess (D) that served as the sample compartment. The upper section consisted of a flat plate (E) with tapered holes (F and F') near its ends and a bolt (G) threaded through its center into a smaller plate (H). The latter plate fit snugly into the sample compartment in plate (A). The vertical rods (C and C') in the lower section of the cell coincided with the tapered holes (F and F') in the upper section. The 2 sections could be held together by passing the vertical rods (C and C') through the holes (F and F') and moving the lower section laterally until the enlarged heads of the rods were located over the narrow sections of the tapered holes. Then bolt (G) could be screwed downwards so that plate (H) pressed the sample against the flat surface of the ZnSe hemicylinder. Evaporation from the sample was prevented by sealing all the space between plates (A) and (H) with silicone gel and Teflon tape.

The sample cell was held by the rods (I and I') in the ATR assembly. This assembly was fixed in the sample chamber of an FTIR spectrometer (Perkin-Elmer Model 1850) having a mercury-cadmium-telluride (MCT) photoconductive detector cooled by liquid nitrogen. The angle of incidence of the infrared beam on the flat surface of the ZnSe hemicylinder was set at 45° with a goniometer. The mirrors of the ATR accessory were adjusted to maximize the energy throughput (Mulla et al. 1985).

The final spectrum of each sample consisted of 250 scans collected at a nominal resolution of 0.5 cm^{-1} with the interval set at 0.1 cm^{-1}. All sample spectra were recorded in a single ratio mode. A spectrum of the empty cell (background) was first recorded and stored in the spectrometer before each sample spectrum was scanned. The sample spectrum was automatically ratioed to the background spectrum that had just been recorded. The sample compartment of the

ported the filter) there were concentric grooves which led, via radial grooves, to a small stainless-steel draintube (J). After the filter (G) and O-ring (E') were put in place and the base (I) was screwed onto the barrel (F), 3 mL of the montmorillonite suspension was poured into the barrel. Then the barrel was screwed onto the cap (D) and N$_2$ gas was admitted to the pressure assembly. The pressure of the N$_2$ gas was maintained at the selected value within a variance of 0.007 bar ($\approx$0.01 psi) with a high-precision pressure regulator.

At each applied pressure, the montmorillonite-water system was allowed to equilibrate for approximately 76 h with the water in the draintube on the underside of the filter. Note that, at equilibrium:

$$\Pi = P - P_a \qquad [6]$$

where P is the absolute pressure. This procedure assured a high degree of orientation of the basal planes of the montmorillonite layers and modeled the experimental condition of previous work relating Π and λ (Viani et al. 1983, 1985; Wu et al. 1989; Zhang et al. 1995).
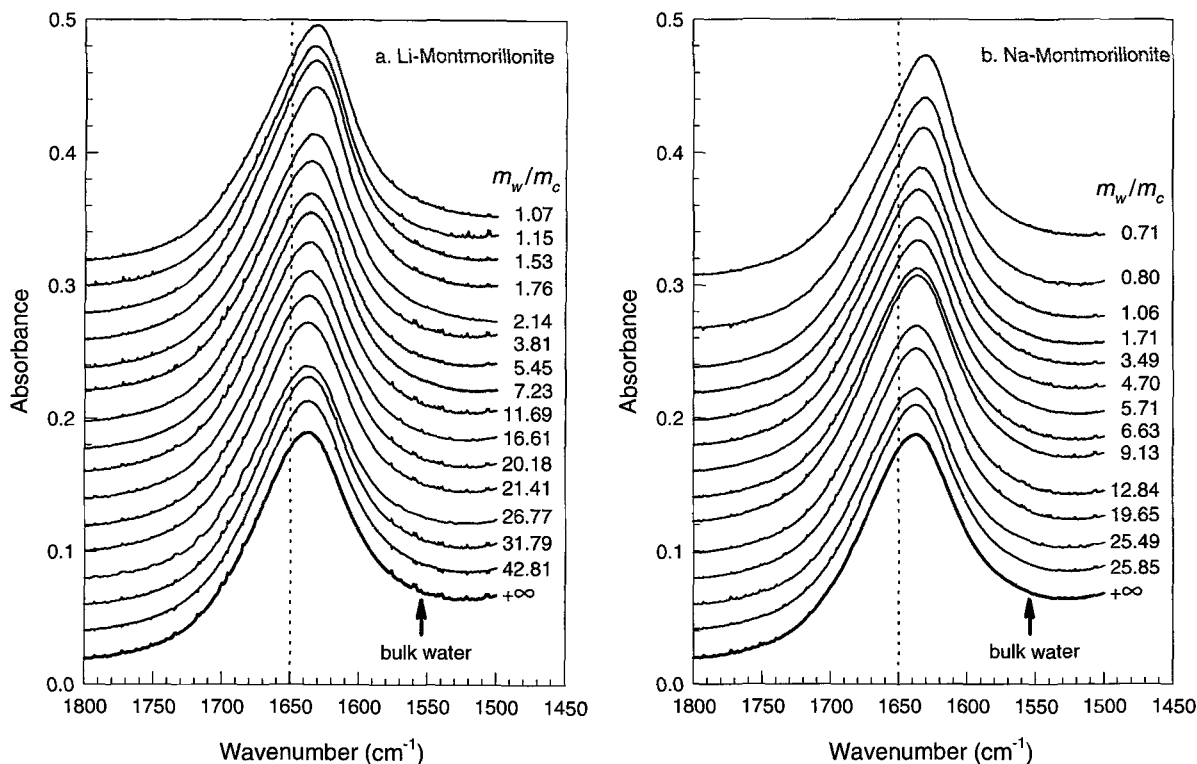
Figure 5. ATR-FTIR spectra of (a) Li-montmorillonite, and (b) Na-montmorillonite in equilibrium with the bulk water at different applied pressures. The spectra are stacked up by 0.02 absorbance units.

spectrometer was well-purged with dry air, aided by additional flowing N_2 gas, before both background and sample scanning. This procedure was necessary to obtain high quality spectra that did not require any smoothing of the data. The spectroscopic data were analyzed using Grams/386 software (Galactic Industries Corporation, Salem, New Hampshire, 1993). The frequency of each peak was determined precisely under identical conditions by the peak-pick program of the software.

RESULTS AND DISCUSSION

Figure 3 is a plot of Π vs. m_w/m_c and Figure 4 of $\ln(\Pi + 1)$ vs. m_c/m_w. The plots in Figure 3 obey Equation [2] and the plots in Figure 4 obey the logarithmic form of this equation provided appropriate values for the parameters α and B are used. Note from Figure 4 that there are breaks in the best-fitting regression lines when $m_c/m_w \cong 0.3$ ($m_w/m_c \cong 3.3$). This means that the parameters α and B in the equations change at that value of m_c/m_w. Values for these parameters are reported in Table 1. Sections of the respective graphs below the break are plotted with dashed lines and sections of the graphs above the break are plotted with solid lines. Breaks of this kind have been observed before (Low 1980).

Observe from Figure 4 that, for Li-montmorillonite, 2 data points are on a linear extension of the dashed line. It is assumed by the authors that the samples represented by these points were in a metastable state. A metastable state has been observed before for the Na-montmorillonite (Low 1980).

A sudden change in the slope of the relation between $\ln(\Pi + 1)$ and m_c/m_w indicates a change of phase of the water in the montmorillonite-water system. The change of phase is accompanied by a corresponding change in molecular arrangement. The following evidence supports such a change and verifies the connection between Π and the structure of the interlayer water. The connection between Π and the structure of the layers of montmorillonite is addressed elsewhere (Yan, Roth and Low 1996).

Bending Frequency of Interlayer Water

Presented in Figure 5 are the observed FTIR-ATR spectra in the range 1800–1500 cm⁻¹. Data for the graphs in Figures 6 and 7 were obtained from these spectra. The equations describing the respective graphs are:

$$\nu_2/\nu_2{}^\circ = F \exp\left(\frac{\beta}{m_w/m_c}\right) = F \exp(\beta \, m_c/m_w) \quad [7]$$

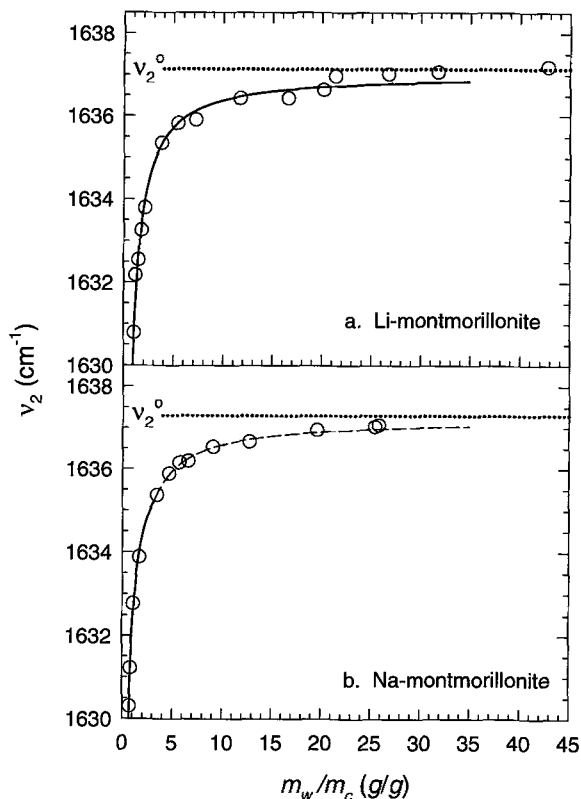and the logarithmic form of this equation. In Equation

Figure 6. The relation between v_2 and m_w/m_c for (a) Li-montmorillonite, and (b) Na-montmorillonite. In (b) the dashed line is the range of higher water content and the solid line is the range of lower water content.

Figure 7. Relation between $\ln(v_2/v_2^\circ)$ and m_c/m_w for (a) Li-montmorillonite, and (b) Na-montmorillonite. In (b) the dashed line is the range of higher water content and the solid line is the range of lower water content.
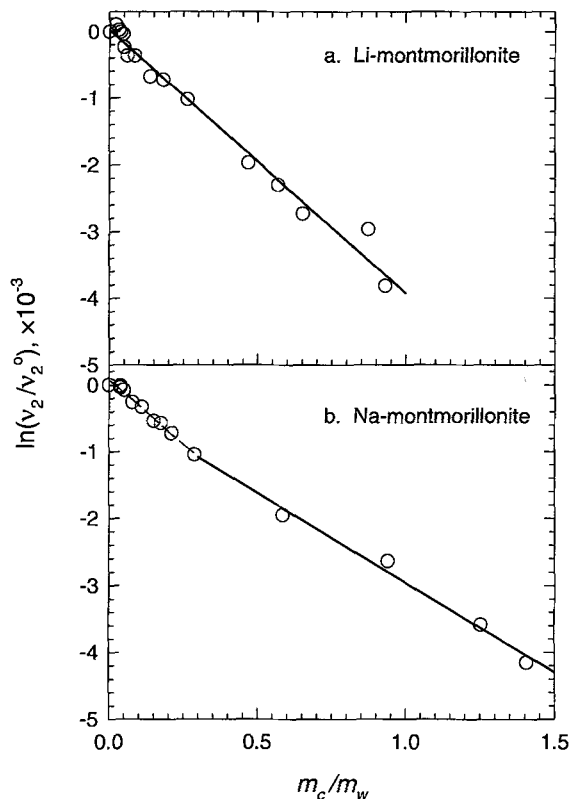
[7], v_2° is the bending frequency of the bulk water ($m_w/m_c = +\infty$), and F and β are constants that are characteristic of the property and the nature of the montmorillonite. The values of these constants are reported in Table 2. Observe that Equation [7] is identical to Equation [4], provided $F = 1$. In previous papers, this proviso appeared to hold.

Since there is a break in the best-fitting lines for Na-montmorillonite in Figure 7, 2 sets of values of β and F are reported for this clay, one set being applicable below the break and the other set being applicable above the break. Note that the value of F is about 1.0 for Li-montmorillonite. However, $F = 1.0$ only below the break, that is, in the range of higher water content, and $F < 1.0$ above the break for Na-montmorillonite. As before, the dashed lines in Figures 6 and 7 represent the data below the break in the log-

arithmic curve and the solid lines represent the data above this break.

Observe from Figure 6 that the water in the montmorillonite-water system is different from bulk water, and that the difference increases as m_w/m_c decreases. If it were the same, v_2 would equal v_2° at all values of m_w/m_c. It should be noted here that several other investigators (Fripiat et al. 1960; Serratosa 1960; Russell and Farmer 1964; Jorgensen 1968; Van der Marel and Beutelspacher 1976; Poinsingon et al. 1978; Johnston et al. 1992), working with relatively dry clay films, also observed a decrease in v_2 with decreasing in m_w/m_c.

Breaks in the relation between v_2 and m_c/m_w were also observed at about the same m_c/m_w by Mulla et al. (1985). Such breaks provide evidence for a sudden structural reorganization of the water molecules in the

Table 2. Statistically determined parameters in Equation [7].

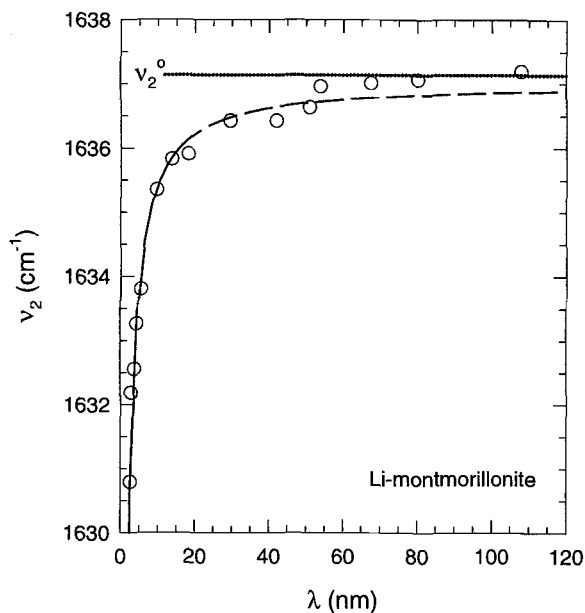| Clay		$\beta \times 10^3$	F	R^2
Li-montmorillonite		−3.9401	1.0000	0.98
Na-montmorillonite	—below break	−3.8642	1.0000	0.99
	—above break	−2.6743	0.9997	0.99

Figure 8.   The relation between ν_2 and λ for Li-montmorillonite. Note that the dotted line represents the extrapolated values of λ.
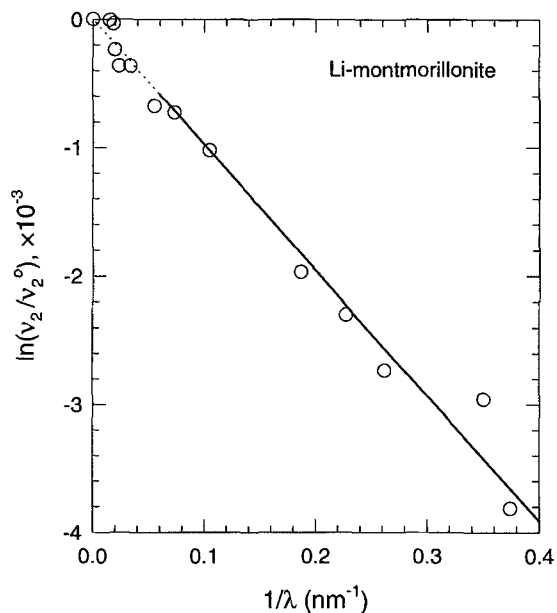

Figure 9.   Relation between $\ln(\nu_2/\nu_2^\circ)$ and $1/\lambda$, for Li-montmorillonite. Note that the dotted line represents the extrapolated values of λ.

montmorillonite-water system. In another paper (Yan, Roth and Low 1996), it is shown that the rate of change of the Si-O stretching frequency in montmorillonite layers changes at the same m_c/m_w. This is the m_c/m_w at which the relation between $\ln(\Pi + 1)$ and m_c/m_w exhibits a break. We believe, therefore, that Π is affected by H-O-H vibrations in the interlayer water and Si-O vibrations in the layers of the montmorillonite.

The bending frequency, ν_2, decreases as the hydrogen bonds of water become weaker (Greinacher et al. 1955; Pimentel and McClellan 1960; Falk 1984; Grodzicki and Piszczek 1994). Consequently, from the Figures 6a and 6b, we conclude that the hydrogen bonds of the interlayer water become weaker as m_w/m_c decreases. This conclusion is supported by the upward shift in the O-D stretching frequency (Sallé de Chou et al. 1980; Fu et al. 1990; Gan 1990), and the downward shift in the molar absorptivity at the frequency of O-D stretching (Mulla and Low 1983).

Several investigators (Russell and Farmer 1964; Poinsingon et al. 1978; Johnston et al. 1992) have concluded that the shifts of both bending frequency and stretching frequency of the interlayer water are attributable to increasing polarization of water molecules by exchangeable cations as m_w/m_c decreases. It should be pointed out, however, that theoretical studies have led to opposite conclusions (Sartori et al. 1958; Sadlej and Sadlej 1977; Falk et al. 1986), and the magnitude and sign of shifts of ν_2 induced by cations themselves are quite uncertain (Falk 1984). We favor the view that

the change we observed in ν_2 (Figures 5–7) is due to perturbation in the structure of vicinal water by the surfaces of montmorillonite.

Statistical mechanical simulations of silicate-water systems show that the vicinal water differs substantially from bulk water in the static orientation of molecular dipole moments and the rate of relaxation of these moments (Mulla, Cushman and Low 1984; Mulla, Low et al. 1984). Hydrogen bonding in the first 2 layers of water near the surface significantly differs from that in bulk water. Also, the results of molecular dynamics simulation by Kjellander and Marcelja (1985) have shown that the electric fields associated with discrete surface charges strongly orient neighboring water molecules and, thereby, weaken the hydrogen bonds.

Bending Frequency of Interlayer Water vs. Interlayer Distance

The relation between λ and Π has been established in this laboratory (Viani et al. 1983, 1985; Wu et al. 1989; Zhang et al. 1995). Zhang and Low (1989) and Fu et al. (1990) have presented data showing that a linear relation exists between λ and m_w/m_c up to $m_w/m_c \cong 5$. To obtain values of λ at higher values of m_w/m_c, we extrapolated the linear relation they observed. Thus, we could obtain Figures 8 and 9. The dotted lines in these figures represent the range in which extrapolated values of λ were used. The graphs in Figures 8 and 9 are described by the equation:
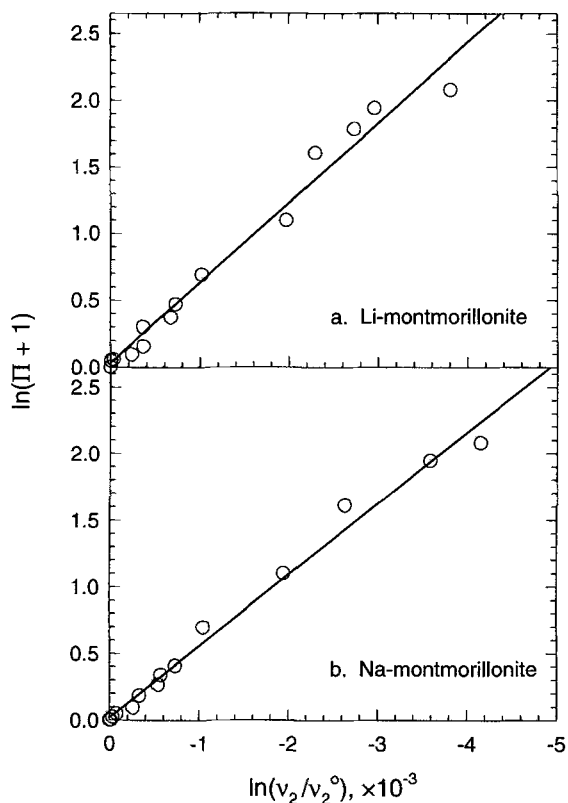
Figure 10.   Relation between the $\ln(\Pi + 1)$ and $\ln(v_2/v_2^\circ)$ for (a) Li-montmorillonite, and (b) Na-montmorillonite.

$$v_2/v_2^\circ = c \exp (\gamma/\lambda) \qquad [8]$$

and by the logarithmic form of this equation, respectively, with $c = 1.0$ and $\gamma = -9.774 \times 10^{-3}$. We did not obtain similar graphs for Na-montmorillonite since, as shown by Zhang and Low (1989), there is a range of m_w/m_c in which 2 values of λ are observed.

Relation of Bending Frequency of Water to Swelling Pressure

To demonstrate the validity of Equation [5] with $J_i/J_i^\circ = v_2/v_2^\circ$ we have included Figure 10. Note that a linear relation is found between $\ln(\Pi + 1)$ and $\ln(v_2/v_2^\circ)$ for both Li- and Na-montmorillonite. We recognize that this relation does not necessarily mean that the variables involved are directly related to each other. However, it does provide strong support for the conclusion that perturbation of the interlayer water by the montmorillonite layers is primarily responsible for both the development of Π and the departure of v_2 from v_2°.

CONCLUSIONS

In summary, we have shown that the bending frequency, v_2, of interlayer water in montmorillonite differs from that of bulk water and that this difference is

significant. Also, we have shown that v_2, like other water properties, is exponentially related to the water content of the montmorillonite. Most importantly, we have shown that a linear relation exists between $\ln(\Pi + 1)$ and $\ln(v_2/v_2^\circ)$ in any given montmorillonite-water system. This finding supports the postulate that the surfaces of montmorillonite induce an in-depth perturbation in the vicinal water and that the perturbation is mainly responsible for the interlayer force (swelling pressure) in the clay-water system.

ACKNOWLEDGMENTS

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