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VIBRATIONAL PROBE STUDIES OF WATER INTERACTIONS WITH MONTMORILLONITE

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Abstract—Interaction of water with montmorillonite exchanged with Na^+, K^+, Co^{2+}, and Cu^{2+} cations as a function of water content was examined using an FTIR/gravimetric cell designed to collect spectroscopic and sorption data simultaneously. Correlation of water desorption isotherms with infrared spectra of the clay-water complex showed that the position of the HOH bending band of water decreased as a function of water content. The largest decreases in frequency were observed for Cu^{2+} and Co^{2+}; smaller decreases were found for Na^+ and K^+. In addition, the molar absorptivity of sorbed water increased upon decreasing the water content. The decrease in frequency and the concomitant increase in molar absorptivity were attributed to polarization effects on the sorbed water molecules by exchangeable cations. The interference fringes of a self supporting clay film permitted d-spacings to be determined optically and, therefore, changes in frequency, molar absorptivity, and water sorption behavior to be related directly to changes in interlayer spacing. The d-spacings obtained from the interference fringes were consistently larger by approximately 0.5 Å than those determined using powder XRD.

Key Words—Cation exchange, Desorption isotherm, FTIR, Gravimetric, Montmorillonite, Physisorption, Water

INTRODUCTION

Since the pioneering work of Mooney *et al.* (1952a, 1952b), the behavior of water molecules on smectite surfaces has continued to attract considerable attention. When less than three molecular layers of water are present in the interlamellar region, the structure of sorbed water on smectites has been shown to be influenced predominantly by exchangeable cations (Mooney *et al.*, 1952b; Clementz *et al.*, 1973, 1974; Prost, 1975; McBride, 1982; Sposito and Prost, 1982; Sposito *et al.*, 1983; Bidadi *et al.*, 1988; Grandjean and Laszlo, 1989; Kogelbauer *et al.*, 1989; Hall and Astill, 1989; Trillo *et al.*, 1990; Fu *et al.*, 1990; Delville *et al.*, 1991; Tinet *et al.*, 1992). Spectroscopic investigations of smectite-water interactions (Prost, 1975; Sposito and Prost, 1982; Brown and Kevan, 1988; Weiss *et al.*, 1990a; Bank *et al.*, 1991; Tinet *et al.*, 1992) suggest that two distinct environments of sorbed water are present: 1) water molecules coordinated directly to exchangeable metal cations, and 2) physisorbed water molecules occupying interstitial pores, interlamellar spaces between exchangeable metal cations, or polar sites on external surfaces.

On the basis of NMR and ESR (McBride and Mortland, 1974; McBride *et al.*, 1975; McBride, 1982; Brown and Kevan, 1988; Grandjean and Laszlo, 1989; Kogelbauer *et al.*, 1989; Delville *et al.*, 1991), complex dielectric permittivity and neutron scattering data (Sposito and Prost, 1982), and other dielectric measurements (Fripiat *et al.*, 1965; Bidadi *et al.*, 1988), water molecules coordinated to metal cations on a clay mineral surface are considered to be in less mobile, restricted environments relative to those in bulk water. This molecular picture of coordinated water in the interlamellar region is consistent with vibrational spectroscopic studies of water sorbed on smectites (Farmer, 1978). Russell and Farmer (1964), for example, found that the OH stretching and bending bands in the infrared (IR) spectra of water sorbed on montmorillonite and saponite were perturbed on going from higher to lower hydration states of these smectites. In the case of the HOH bending band (ν_2 mode) in the 1610 to 1640 cm^{-1} region, the frequency decreased and the molar absorptivity increased upon dehydration of the clay mineral. A similar result was reported by Poinsignon *et al.* (1978), who observed that the molar absorptivities of the OH stretching and bending bands in the IR spectrum of sorbed water depended strongly on the hydration energy of the exchangeable metal cation and on both the water content and surface charge density of the clay mineral.

In the present study, the use of the ν_2 band of sorbed water is examined as a molecular probe of smectite-water interactions by establishing a relationship between vibrational spectroscopic data and 1) the surface coverage of water and 2) the observed basal spacing. Although previous IR studies of water-smectite systems (Russell and Farmer, 1964; Poinsignon *et al.*, 1978; Farmer, 1978) have shown that water coordinated to exchangeable metal cations is distinct from physisorbed or bulk water, the correlation of IR data with the amount of water sorbed has not been determined. Moreover, it is not known how changes in the basal spacing of a smectite influence the vibrational properties of sorbed water molecules. Recently, Fu *et*

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al. (1990) have combined water desorption isotherms, X-ray diffraction (XRD), and transmission IR spectral data for Na-Wyoming montmorillonite to study the structure of sorbed H_2O (or D_2O) at water contents above 0.01 kg/kg clay. From XRD they inferred stepwise desorption of water and, from IR measurements, a corresponding increase in the frequency of the OD stretching vibration. Fu *et al.* (1990) interpreted their results as evidence of increasing structural disorder in sorbed water along the desorption isotherm. Laperche *et al.* (1990) have applied solid-state NMR and XRD simultaneously to investigate the coordination of water molecules to $^{23}Na^+$, $^{133}Cs^+$, and $^{111}Cd^{2+}$ on vermiculite during stepwise water sorption. They concluded that the chemical shift of the exchangeable cation reported sensitively on the competition between clay mineral surface oxygens and water molecules for cation coordination sites. In this paper, we examine the water-smectite interaction via the simultaneous measurements of the HOH bending vibration and the basal spacing during water desorption from Na-, K-, Co- and Cu-exchanged montmorillonite.

EXPERIMENTAL METHODS

Preparation of self-supporting clay films

The samples studied were SAz-1 (Apache County, Arizona) and SWy-1 montmorillonite (Crook County, Wyoming), obtained from the Source Clays Repository of The Clay Minerals Society (Van Olphen and Fripiat, 1979). Prior to size fractionation, a homoionic Na-montmorillonite clay suspension was prepared by placing 10 g of the raw clay in one liter of 0.5 M NaCl. The Na-montmorillonite suspension then was washed free of excess salts by repeated centrifugation with distilled-deionized water. The <0.5 μm size fraction (ESD) was collected by centrifugation. Homoionic clay suspensions of Cu-, Co-, and K-exchanged SAz-1 montmorillonite were prepared by adding approximately 0.7 liter of 0.05 M solution of the metal chloride to the salt-free clay suspension (volume $\approx$ 0.3 liter), such that the total volume was 1.0 liter. The final pH value of these suspensions was 5. The washing and size fractionation steps were completed within a 24 hr period to minimize degradation of the clay.

Self-supporting clay films were prepared by washing 20 ml of the stock montmorillonite clay suspensions free of excess salts. The solids concentration of the suspension was diluted to 2.5 mg clay/(g suspension). Aliquots of 1.0 ml of this suspension were deposited on a polyethylene sheet and allowed to dry. The dry clay films were then peeled off the polyethylene sheet as self-supporting clay films. These clay films were approximately 2.5 cm in diameter with a mass between 3.1 and 3.4 mg, corresponding to a cross-sectional density of about 0.65 mg/cm^2. The cation exchange capacity of the clay films was determined by placing a known amount (3 to 5 mg) of the dry clay film in 5 ml of 0.25 M $MgCl_2$ and allowing the suspension to stand for 12 hours. A portion of the supernatant solution was removed for analysis of Na and Cu. This procedure was repeated twice. The cation exchange capacities of the clay films were 0.99 ± 0.02 $mmol_c$ g^{-1} for Na-SAz-1 and 1.11 ± 0.02 $mmol_c$ g^{-1} for Cu-SAz-1.

FTIR/gravimetric cell

For the simultaneous FTIR/gravimetric measurements, FTIR spectra were obtained using a Bomem DA3.10 FTIR spectrometer equipped with a MCT detector ($D^* = 3.13 \times 10^9$ cmHz$^{0.5}$ and a low-frequency cutoff of 400 cm^{-1}) and a KBr beamsplitter (for a discussion of FTIR methods in surface studies, see Johnston, 1990). The Bomem DA3.10 spectrometer was controlled through a general-purpose-interface-bus (IEEE-488) interfaced to a DEC μVAX-II computer. The unapodized resolution for the FTIR spectra was 2.0 cm^{-1}.

A 15 cm pathlength gas cell fitted with two ZnSe windows, Viton® O-rings, and two stopcocks was modified to interface with a Cahn® controlled-environment Model D200-01 electrobalance (Figure 1). The modified gas cell allowed FTIR spectra and gravimetric data to be collected simultaneously. A complete description of the cell is given elsewhere (Johnston *et al.*, 1991, 1992). The cell was connected to a gas/vacuum manifold that permitted the atmosphere in the cell to be controlled and the pressure to be monitored. A self-supporting homoionic montmorillonite clay film was placed on a 0.2 mm Pt hangdown wire in the Cahn® electrobalance. The modified gas cell was mounted on a NRC optic table and was positioned using NRC x-y-z translational stages that permitted adjustment of the cell. Mounting the cell on the optic table mechanically isolated the electrobalance assembly from vibrations originating from operation of the FTIR spectrometer and from other sources. The cell was positioned such that the clay film was centered on, and nearly perpendicular to, the incident modulated IR beam in the sample compartment.

Desorption isotherms

Desorption isotherms were obtained by placing 1.5 ml of water in one of the hangdown tubes of the Cahn® balance after the clay film had been mounted and tared on the balance. The water was frozen by placing a dewar flask of liquid nitrogen around the hangdown tube. The Cahn® balance and FTIR cell were then evacuated to 0.005 torr using a roughing pump. At this point, the isolation valve between the Cahn® balance/IR cell and the vacuum manifold was closed and the liquid nitrogen dewar was removed. The water was allowed to equilibrate slowly and the pressure inside the Cahn® balance/IR cell was determined using a Baratron gauge. The clay film was allowed to equili-

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brate for 24 hours in the presence of a small excess of liquid water to obtain a relative vapor pressure (P/P_o) value near 1.0. At this point, the mass of the sample, the pressure inside the cell, and the temperature were recorded along with the FTIR spectrum of the clay film. The mass of the clay film was recorded every 10 to 30 seconds using a Zenith® 286 computer interfaced to the Cahn® D200 balance. After the clay film had come to equilibrium, a small amount of vapor was removed from the cell by opening the isolation valve and the system was allowed to re-equilibrate. At a given partial pressure of water, the mass of the clay film was monitored electronically until the mass changed less than a few percent within a 20 min period. Typically, at least one hour of equilibration time was required for each data point.

Optical determination of clay film thickness and d-spacing

Interference fringes were present in the FTIR spectra of the clay films because of optical interference among internally reflected IR waves inside the clay film. The distance between the fringes varied as a function of the water content corresponding to changes in the basal spacing of the clay mineral. The thickness of the clay film was determined according to the equation (Griffiths and deHaseth, 1986):

$$b = \frac{1}{2n}\frac{N}{(\nu_1 - \nu_2)} \quad (1)$$

where b is the thickness of the sample, N is the number of interference fringes over the wavenumber range ($\nu_1 - \nu_2$), and n is the refractive index of the clay film. Mehmel (1937) observed an increase in the index of refraction of montmorillonite from 1.49 to 1.555 upon drying the clay to 105°C. A fixed value of 1.55 was used in this study. This approximation should underestimate the thickness of the clay film at high water contents but should be more accurate at low water contents. The dry mass of the clay film was determined by plotting the intensity of the OH bending or stretching band *vs* the mass of the sample and extrapolating the plot to zero band intensity. The cross-sectional area of the clay film was controlled by cutting the clay film precisely into 1.2 cm × 1.2 cm squares.

The basal or d-spacing was calculated from the optical interference fringes using the expression:

$$\text{d-spacing} = \frac{b}{\frac{m_{NaX}N_A A_1}{MW_{NaX}A_2}} \quad (2)$$

where:

m_{NaX} = dry mass of Na-clay film (g clay/film)

N_A = Avogadro constant = 6.0225×10^{23} (1/mol)

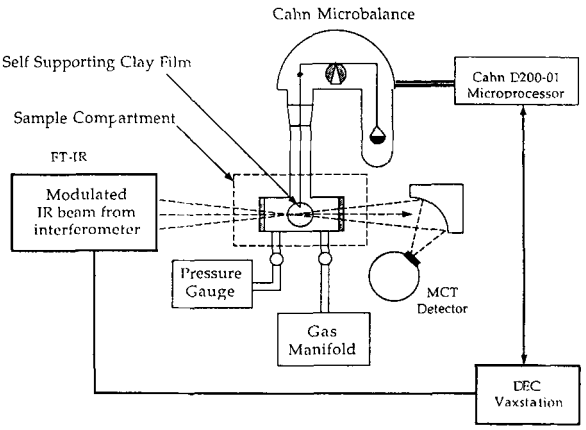


Figure 1. Schematic of the *in situ* FTIR/gravimetric cell showing the following: gas manifold and pumping station, Cahn® D200-01 electrobalance, 16 cm path length gas cell fitted with two 50 × 3 mm ZnSe windows, Viton O-rings, two Kontes stopcocks, and a 164/45 ground glass joint used to interface the hangdown tube of the Cahn® balance with the sample compartment of the Bomem DA3.02 spectrometer.

A_1 = area of unit cell (a·b) (Å²/unit cell)

MW_{NaX} unit-cell mass of Na-clay = 744 (g/mol)

Molecular mass based on chemical analysis of SAz-1 from Laird et al. (1989)

A_2 = cross-sectional area of clay film = 1.44 (cm² clay film)

b = measured thickness of clay film (Å/clay film)

Measurement of molar absorptivity

The surface concentration of water sorbed on the clay films was determined using the Bouguer-Beer-Lambert law ("Beer's law"):

$$A(\nu) = \epsilon(\nu)cd = \ln\left(\frac{I_o(\nu)}{I(\nu)}\right) \quad (3)$$

where $A(\nu)$ is the absorbance of the band of interest, $\epsilon(\nu)$ is the molar absorptivity at wavenumber ν (cm²/mmol), c is the concentration of water (mmol/cm³), d is the thickness of the clay film (cm), $I_o(\nu)$ is the intensity of the incident beam, and $I(\nu)$ is the intensity of the transmitted beam. For water sorption on thin films, it is convenient to replace the quantity (cd) with $\bar{c}$ which has units of mmoles/cm² and corresponds to the number of IR absorbers per unit area:

$$\bar{c} = cd \text{ (mmol/cm}^2\text{)} \quad (4)$$

$$= \text{(mmol water)/(cm}^2\text{ clay film)}$$

$$= \frac{(m_{cs} - m_c)}{(a_c M)} \quad (5)$$

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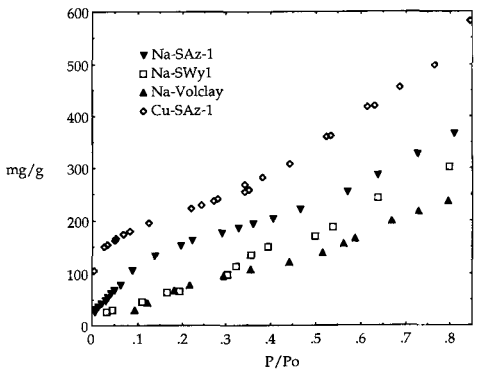


Figure 2. Desorption isotherms of water from self-supporting clay films of Na-SAz-1, Na-SWy-1, and Cu-SAz-1 obtained at 24°C. For comparison, the desorption isotherm of water from a Na-Volclay (Mooney *et al.*, 1952a, 1952b) is shown. The amount of water sorbed per unit mass of dry clay in mg of sorbed water per gram of dry clay is plotted against the relative vapor pressure of water (P/P_o) on the x-axis.

where m_{cs} is the total mass of the clay film (combined mass of clay and water) in mg, m_c is the dry mass of the clay film in mg, a_c is the area of the clay film in cm^2, and M is the molecular mass of the water. Given the measured peak height of a selected water band, the molar absorptivity can be obtained:

$$\epsilon(\nu_{max}) = \frac{A(\nu_{max})_{peak\ height}}{\bar{c}} \quad (6)$$

XRD analysis of d-spacings

X-ray powder diffraction (XRD) patterns were obtained using a Nicolet diffractometer. Samples were scanned at 2° 2Θ min^{-1} using CuK_α radiation. The XRD patterns were collected in a controlled atmosphere at the desired P/P_o value by maintaining a positive pressure of air equilibrated at the target P/P_o value flowing over the sample.

RESULTS

Desorption isotherms of water from Na- and Cu-exchanged SAz-1 and Na-SWy-1 montmorillonite are

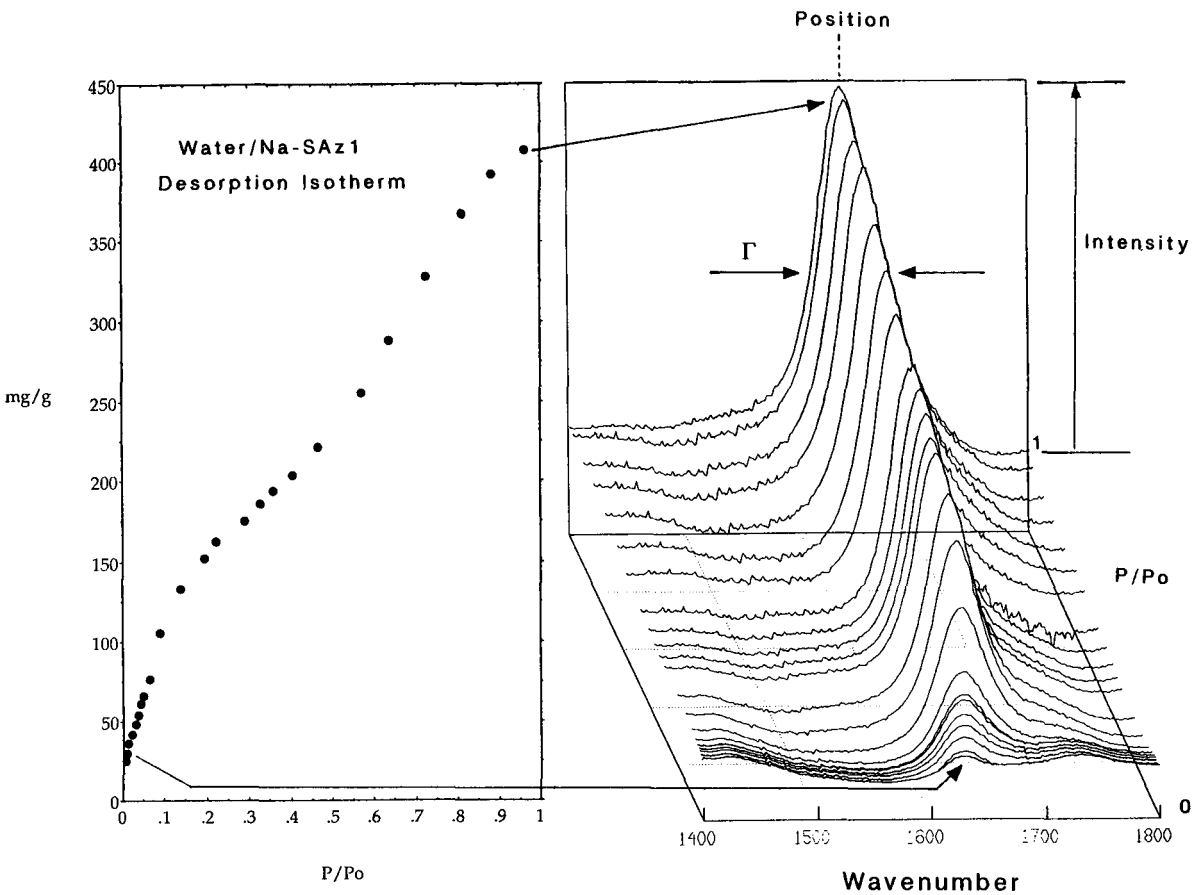


Figure 3. Comparison of the desorption isotherm of water from a self-supporting clay film of Na-SAz-1 obtained at 24°C to the FTIR spectra (right side) of water sorbed on the Na-SAz-1 clay film. Each spectrum shown on the right side corresponds to one data point on the desorption isotherm. The offset along the z-axis corresponds to the relative vapor pressure (P/P_o) x-axis on the left-side of Figure 2.

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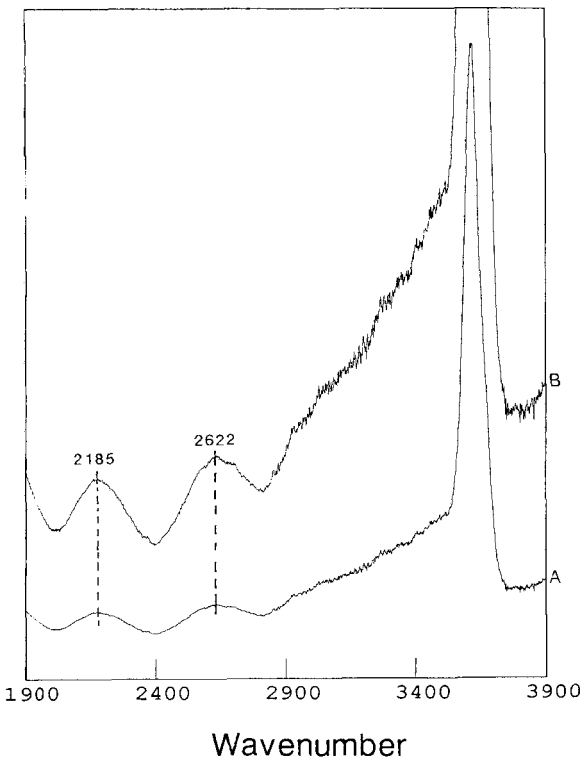


Figure 4. FTIR spectrum of water sorbed on a self-supporting film of Na-SAz-1 at a relative water vapor pressure of 0.008 obtained at 24°C. The interference fringes at 2185 and 2622 cm^{-1} were used to calculate the thickness of the clay film assuming a value of 1.55 for the index of refraction.

compared to the desorption isotherm obtained for a Na-exchanged Volclay (a Wyoming bentonite) by Mooney *et al.* (1952b) in Figure 2. Replacement of Na^+ by Cu^{2+} resulted in increased water sorption. Increased sorption also was observed for the SAz-1 clay as compared to the SWy-1 montmorillonite, evidently reflecting the higher surface charge density of the SAz-1 clay (1.2 $mmol_C\ g^{-1}$) relative to that of the SWy-1 clay (0.9 $mmol_C\ g^{-1}$). Reasonable agreement between desorption data sets for the Na-SWy-1 and the Na-Volclay was obtained in the lower P/P_o range ($0.0 < P/P_o < 0.3$); however, increased uptake was observed for the Na-Swy-1 clay at higher P/P_o. This difference in water uptake may be caused by differences in sample preparation or by the higher surface charge density of the Na-SWy-1 montmorillonite compared to that of the Volclay sample studied by Mooney *et al.* (1952a).

To illustrate the relationship between the desorption isotherms and the spectroscopic data, the Na-SAz-1 isotherm is compared to the corresponding spectroscopic data in Figure 3. For each data point shown on the left side of Figure 2, a corresponding FTIR spectrum was obtained using the FTIR/gravimetric cell (Figure 3). A three-dimensional representation of the FTIR spectra in the 1400 to 1800 cm^{-1} region, shown

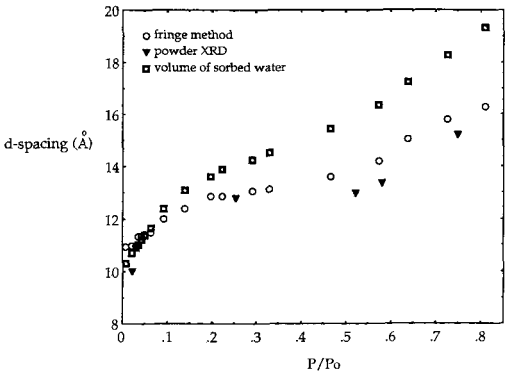


Figure 5. Basal spacing (Å) of a Na-SAz-1 self-supporting clay film plotted as a function of water content (relative vapor pressure of water) determined using the interference fringe method (open circles), powder XRD method (solid diamonds), and the film thickness calculated from the amount of water sorbed (solid triangles).

on the right side of Figure 3, is plotted with the z-axis representing P/P_o. The intensity of the ν_2 band at 1640 cm^{-1} is directly proportional to the amount of water sorbed by the clay. Simultaneous collection of gravimetric and IR spectroscopic data thus provides a method to correlate macroscopic sorption characteristics with molecular vibrational data.

The FTIR spectrum of the Na-SAz-1 montmorillonite film obtained at $P/P_o = 0.008$ is shown in Figure 4, with a scale expanded portion of the spectrum shown. The interference fringes (inset) were used to calculate the d-spacing of the clay film using Eqs. (1) and (2). The influence of water content on the d-spacing of a Na-SAz-1 clay film as determined by the fringe method is shown in Figure 5 (open circles). For comparison, a similar experiment was conducted using a controlled environment XRD mount; the data are also shown in Figure 5 (closed triangles). The fringe-method overestimated the d-spacing of the clay film, probably because of a void volume in the clay film created by imperfect stacking of the clay platelets. A third estimate of film thickness was obtained using the mass of water sorbed on the clay film as obtained from gravimetric data. If the sorbed water molecules are distributed uniformly between the clay layers, the d-spacing of the clay film can be determined (closed triangle in Figure 5). The fact that higher d-spacings were obtained using this last method suggests that multilayer water sorption occurred on external surfaces at water contents corresponding to $P/P_o > 0.1$.

The wavenumber position for the ν_2 band of water sorbed on SAz-1 montmorillonite exchanged with Na^+, K^+, Co^{2+} and Cu^{2+} is plotted in Figure 6 as a function of water content expressed as the average number of water molecules per metal cation. At higher water contents (>10 water molecules/metal ion), the position of

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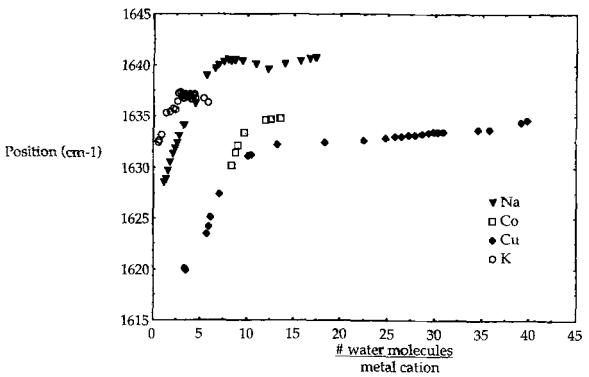


Figure 6. Position of the ν_2 band of water sorbed on SAz-1 montmorillonite exchanged with Na^+, K^+, Co^{+2} and Cu^{+2} plotted as a function of water content expressed as the number of water molecules sorbed per exchangeable metal cation.

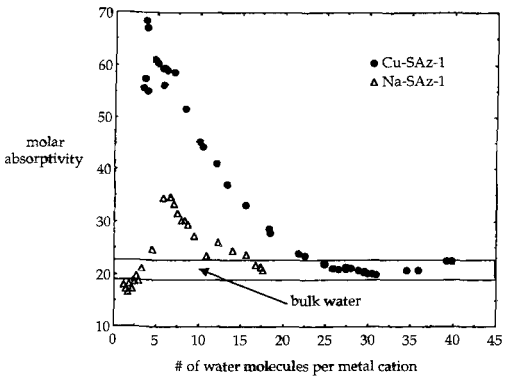


Figure 7. Change in the molar absorptivity of the ν_2 band of water sorbed on SAz-1 montmorillonite exchanged with Na^+ and Cu^{2+} plotted as a function of water content expressed as the number of water molecules sorbed per exchangeable cation.

the ν_2 band was relatively unchanged. The high water content limit of the ν_2 band position was between 1640 and 1624 cm^{-1} in the case of Na-SAz-1 and ranged from 1633 to 1635 cm^{-1} for Cu-SAz-1. At less than 10 water molecules per Cu^{2+} or less than 6 water molecules per Na^+, the position of the ν_2 band decreased in agreement with previous IR studies of water sorbed on smectite (Russell and Farmer, 1964; Poinsignon *et al.*, 1978). Although the same general behavior was observed for the Na- and K-exchanged montmorillonite samples, the slight decrease in frequency of the H-O-H bending band of water sorbed on the Na- and K-exchanged clays was not observed for the divalent-exchanged clays.

The molar absorptivity of the ν_2 band of water sorbed on Na- or Cu-SAz-1 determined using Eq. (6) is shown in Figure 7 as a function of water content. At high water content (>20 water molecules per cation), the molar absorptivity became the same as that of bulk water. At lower water content, however, the molar absorptivity increased until the H_2O/cation ratio reached 6. In comparison to water sorbed on Cu-SAz-1, a smaller increase was observed for the Na-exchanged clay film. A maximum molar absorptivity of 35 cm $mmol^{-1}$ occurred at a (H_2O/Na^+) ratio of 6. Upon reducing the water content further, the molar absorptivity value decreased to a value slightly less than that of bulk water.

DISCUSSION

The water desorption isotherms obtained in the present study are in agreement with published desorption isotherms for water on smectite (Mooney *et al.*, 1952a). Recently, Hall and Astill (1989) reported adsorption isotherms for water on SWy-1 montmorillonite exchanged with Ca, Li, Na, and K that show that considerably more water is present in the desorption isotherm at a given P/P_o than in the adsorption isotherm (i.e., hysteresis). A similar result was reported long ago by Mooney *et al.* (1952a), who showed that desorption isotherms were reproducible, but adsorption isotherms depended strongly on the initial water content and were, in general, not reproducible.

The decrease in basal spacings of the Na-SAz-1 clay film upon lowering the water content agrees well with published studies (Mooney *et al.*, 1952b; Fripiat *et al.*, 1965; Ormerod and Newman, 1983). A novel feature of the present data is, however, that d-spacings were determined optically from the interference fringes of a self-supporting clay film. The d-spacings obtained from the interference fringes, however, were systematically larger by approximately 0.5 Å than those determined using powder XRD. Comparison of the d-spacings obtained using the two methods at the lowest water content (corresponding to $P/P_o = 0.02$) indicates that the void volume of the self-supporting clay film was about 9% assuming that the "true" d-spacing of the clay film was 10 Å, as determined from the powder XRD measurements. In comparison, the d-spacing of the clay as determined from the amount of water sorbed agreed well with the optical and XRD measurements at low water contents. Upon increasing the water content (above $P/P_o = 0.1$), however, the water-sorption d-spacing estimates were systematically larger than those determined using the other two methods. This result provides evidence that multiple layers of water molecules were sorbed on the external surfaces of the clay film (Ormerod and Newman, 1983; Trillo *et al.*, 1990). The fringe method provides a reasonable estimate of the d-spacing with an estimated error of ±0.5 Å.

A decrease in frequency of the ν_2 band upon reducing the water content has been attributed to decreased hydrogen bonding among sorbed water molecules (Russell and Farmer, 1964), increased polarization effects by exchangeable cations (Poinsignon *et al.*, 1978), and a decreased basal spacing of the clay. Upon dehydra-

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tion, the more labile water is removed from the interlamellar region, leaving water molecules that are coordinated to the exchangeable metal cations and thus reducing intermolecular interactions among water molecules. In addition, the remaining water molecules are polarized by the exchangeable cation. A decrease in the position of the ν_2 band generally accompanies an increase in the positions of the ν_1 and ν_3 (O-H stretching bands). The position of the OH stretching bands could not be determined unambiguously in this study because of significant overlap and broadening of the OH stretching bands both with each other and with the structural ν(O-H) band at 3630 cm^{-1}. Fu *et al.* (1990) avoided this problem by replacing H_2O with D_2O and found that the position of the ν(O-D) band increased upon lowering the water content of a D_2O–Na-montmorillonite suspension. They proposed that disorder in the clay-water system increased at lower water contents because of strain effects between clay layers. This hypothesis is consistent with our data, in that the environment around partially solvated metal cations should be less ordered than under hydrated conditions. Additional evidence is provided by recent NMR spectroscopic studies of exchangeable cations on montmorillonite (Weiss *et al.*, 1990a, 1990b; Laperche *et al.*, 1990) where the line-broadening observed at low water contents is attributed to a decreased mobility of the cation, and by interactions between the cation and the clay mineral surface itself.

The increase in the molar absorptivity of the ν_2 band of water sorbed on Cu-SAz-1 and Na-SAz-1 (Figure 7) upon dehydration is consistent with the work of Russell and Farmer (1964) and with that of Poinsignon *et al.* (1978). The latter authors attributed the increase in the absorption coefficient of this band (proportional to the molar absorptivity) to an increased polarization of water by the exchangeable cation at low water contents. They found that the absorption coefficients of the OH stretching and bending modes increased as the ionic potential of the exchangeable cation increased. Although Cu^{2+} was not included in their study, a higher molar absorptivity would be anticipated for Cu^{2+} relative to Na^+ on the basis of the ionic potentials of the two cations. One point to emphasize is that a single molar absorptivity value for the ν_2 band of water is not likely for either the Na- or Cu-exchanged SAz-1 montmorillonites. Rather, the observed molar absorptivity depends strongly on the water content of the clay. Our data (Figure 7) do not agree, however, with the data of Mulla and Low (1983) who reported a decrease in the molar absorptivity of the ν_2 band of water sorbed on Na-montmorillonite as the water content decreased. Their data, however, were obtained for dilute aqueous suspensions of Na-montmorillonite having water contents several orders of magnitude greater than those used in this study; thus, a direct comparison cannot be made.

There is general agreement in the literature that the surface acidity of smectites increases at low water contents (Mortland and Raman, 1968; Voudrias and Reinhard, 1986). The decrease in the position of the ν_2 band of water and the corresponding increase in its molar absorptivity upon lowering the water content suggest that one or both of these properties may be used as a diagnostic property to probe the surface acidity of mineral surfaces. It would be useful to examine the position and molar absorptivity of the ν_2 band, and possibly the ν_1 and ν_3 bands, of water sorbed on montmorillonite as a function of surface acidity measured directly. One possibility would be to correlate these diagnostic properties of water with the protonation of NH_4^+ sorbed on smectite (Mortland and Raman, 1968).

CONCLUSIONS

The combined vibrational and gravimetric data indicate that water molecules residing near the surface of montmorillonite are strongly influenced by the type of exchangeable metal cations present on the clay and by the overall water content. At higher water contents (i.e., >15 water molecules per exchangeable metal cation) the vibrational properties of water are similar to those of bulk water. Upon lowering the water content below this threshold value, however, the position of the ν_2 band of water decreases to lower wavenumber values and the molar absorptivity of the ν_2 band increases significantly. During the desorption process, it is assumed that two types of water molecules are present: water molecules directly coordinated to exchangeable metal cations and those occupying void volumes and interstitial pores. Because the latter type of water is not strongly bound to the clay surface, these water molecules are selectively removed during the desorption process. In addition to the perturbations by exchangeable metal cations, the influence of the clay surface on the vibrational properties of interlayer water also becomes more prominent at lower water contents due to a reduction in the interlayer volume. The vibrational spectra obtained at low water contents are dominated by contributions from the water molecules strongly coordinated to exchangeable metal cations. These changes indicate that the water molecules strongly coordinated to the interlamellar cations are polarized. The extent of polarization depends on the type of water content and the nature of the exchangeable cation. A larger influence was seen for Cu^{2+} as compared to that for Na^+ or K^+, resulting from the greater hydration energy of Cu^{2+} relative to those of Na^+ or K^+. Increased polarization of water molecules at low water contents is thought to be associated with the increase in surface acidity at reduced water contents. Thus, the diagnostic properties of water studies here could be used as indicators of the surface acidity of clay minerals.

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