# CHANGES IN THE PROPERTIES OF A MONTMORILLONITE-WATER SYSTEM DURING THE ADSORPTION AND DESORPTION OF WATER: HYSTERESIS[1]

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**Abstract**—Samples of Na-saturated, Upton montmorillonite were prepared with different contents of water ($H_2O$ or $D_2O$) by: (1) adsorption of water from the vapor phase at a specific value of $p/p°$, the relative humidity, (2) adsorption of water from the vapor phase at $p/p° = 1.0$ followed by desorption of the water into the vapor phase at a specific $p/p° < 1.0$, and (3) adsorption of water from the liquid phase followed by desorption of the water into the vapor phase at a specific $p/p° < 1.0$. Water adsorbed initially from the vapor phase was called V-adsorbed water, and water adsorbed initially from the liquid phase was called L-adsorbed water. The water contents of these samples were determined by gravimetric analysis, the $c$-axis spacings by X-ray powder diffraction, the O–D stretching frequencies by IR spectroscopy, and the heats of immersion by differential microcalorimetry. No difference was found between V-adsorbed and L-adsorbed water; however, if the final water content was established by adsorption, the system was in a different state than if the final water content was established by desorption. In particular, hysteresis was observed in the following properties: the relative humidity of the adsorbed water, the O–D stretching frequency in this water, and the degree of order in the stacking of the clay layers. The only property that did not exhibit hysteresis was the heat of immersion. Apparently, hysteresis occurred because the orderliness of the system was not reversible, and, thus, any property that depended on orderliness was hysteretic.

**Key Words**—Adsorption, Desorption, Hysteresis, Infrared spectroscopy, Montmorillonite, Vapor pressure, Water.

## INTRODUCTION

A Na-saturated smectite swells if it is in contact with liquid water until its superimposed layers are ~200 Å apart (Norrish, 1954; Viani *et al.*, 1983); whereas, if it is in contact with water vapor at the same relative humidity as the liquid water, it swells until its superimposed layers are only 7–10 Å apart (Mooney *et al.*, 1952; Glaeser and Méring, 1968; Suquet *et al.*, 1975; Margheim, 1977). This difference in swelling suggests that the state of water adsorbed from the liquid phase may not be the same as the state of water adsorbed from the vapor phase. Water molecules are probably adsorbed collectively as coordinated clusters from the liquid phase but individually from the vapor phase; hence, the two modes of adsorption could produce dissimilar molecular arrangements with dissimilar properties. Inasmuch as water adsorption by smectites is an important phenomenon, we determined by calorimetric, spectroscopic, adsorptive, and X-ray diffraction analyses whether or not the state of the adsorbed water was affected by its mode of adsorption. The present paper reports the results.

## MATERIALS AND METHODS

The clay used in this study was the Upton Na-montmorillonite prepared and characterized by Low (1980)

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and identified by him as Upton #2. Samples of this montmorillonite were brought to different values of $m_w/m_c$, the mass ratio of water ($H_2O$ or $D_2O$) to clay, by the following methods:

1. Duplicate samples of the dry montmorillonite were enclosed in desiccators over saturated salt solutions maintaining different values of $p/p°$, the relative humidity, and allowed to adsorb water vapor at 25°C until equilibrium was achieved.

2. Duplicate samples of the dry montmorillonite were enclosed in a desiccator over pure water and allowed to adsorb water vapor at 25°C until equilibrium was achieved. They were then enclosed in desiccators over saturated salt solutions maintaining different values of $p/p°$ and allowed to desorb water at the same temperature until equilibrium was achieved again.

3. Duplicate samples of the dry montmorillonite were sprayed with sufficient *liquid* water to bring the value of $m_w/m_c$ to ~2 g/g. Thereafter, they were enclosed in desiccators over saturated salt solutions maintaining different values of $p/p°$ and allowed to desorb water at 25°C until equilibrium was attained.

Values of $p/p°$ for the saturated salt solutions with $D_2O$ as solvent were not known. Therefore the $p/p°$ values were assumed to be the same as those for the corresponding solutions with $H_2O$ as the solvent.

The time allowed for equilibration in each method was about 4 weeks. In methods 1 and 2, the water was

adsorbed initially from the vapor state. It will be called V-adsorbed water. In method 3, the water was adsorbed initially from the liquid state. It will be called L-adsorbed water. Method 1 differed from method 2 in that, although they both produced V-adsorbed water, the final equilibrium was attained by adsorption in the former and desorption in the latter. Values of $m_w/m_c$ obtainable by vapor adsorption were too low to be readily attainable by liquid adsorption, i.e., by mixing the dry clay with liquid water. Therefore, appropriate values of $m_w/m_c$ for the L-adsorbed water were obtained by desorption only.

Samples of montmorillonite treated by these three methods were analyzed gravimetrically to determine the respective values of $m_w/m_c$. These values were then plotted against the corresponding values of $p/p°$ to construct the adsorption isotherm for V-adsorbed water and the desorption isotherms for V-adsorbed water and L-adsorbed water.

To determine the $c$-axis spacings corresponding to the different values of $m_w/m_c$ achieved by the three methods, oriented samples were prepared by pipeting 4-ml aliquots of a 3% suspension of the montmorillonite on glass slides (5 cm × 5 cm) and evaporating until $m_w/m_c \simeq 1.0$ g/g. Then, in the following sequence, the oriented samples were: (1) treated as described in method 3 and analyzed by X-ray powder diffraction (XRD), (2) dried over silica gel, treated as described in method 1, and analyzed by XRD again, and (3) treated as described in method 2 and analyzed by XRD a third time. To prevent any gain or loss of water during the XRD analysis, each sample was enclosed in an environmental chamber (Viani *et al.,* 1983) and exposed to water vapor at the same $p/p°$ that existed during the preceding equilibration.

XRD was accomplished with a Siemens X-ray diffractometer using CuKα radiation. Beam intensities were recorded in digitalized form at intervals of 0.04° from 3° to 11°2θ. The digitalized data were collected on magnetic tape and transmitted to a computer where they were corrected for the Lorentz-polarization factor. The single-crystal version of this factor was used. Finally, $c$-axis spacings were computed from the positions of the corrected diffraction peaks by Bragg's law.

All of the above experiments were performed with both $H_2O$ and $D_2O$ as adsorbates; however, in the following spectroscopic experiment, only $D_2O$ was used as adsorbate. It was not feasible to use $H_2O$ in this experiment because O–H stretching in the adsorbed $H_2O$ can be confused with O–H stretching in the montmorillonite. In this regard, note that the O–H stretching frequency increases with the length of the hydrogen (O–H. . .O) bond (Pimentel and McClellan, 1960; Vinogradov and Linnell, 1971). Moreover, because the vibrational frequency of any diatomic molecule is inversely proportional to the square root of the reduced mass of the atoms involved (Herzberg, 1950), the O–

H stretching frequency is 1.36 times the O–D stretching frequency.

To measure the O–D stretching frequency, samples ~0.001 cm thick were prepared by evaporating 1-cm³ aliquots of a 1% suspension of the Na-montmorillonite on AgCl windows (o.d. = 2.54 cm) within the confines of flat, plastic rings that were sealed to the margins of the windows with silicone grease. The samples were brought to their final $D_2O$ contents by the three methods that were used to prepare the corresponding samples for XRD analysis. The upper AgCl windows were then sealed to the tops of the rings with silicone grease. As a result, the samples were enclosed in miniature environmental cells, and no $D_2O$ was allowed to escape from them during spectroscopic analysis.

Transmission spectra of the samples were obtained with a Perkin-Elmer (Model 180) spectrophotometer. The digitalized data were recorded on magnetic tape and transmitted to a computer where they were converted to an x, y format and subjected to a computer program written locally to determine the positions of the O–D absorption peaks at the respective values of $m_w/m_c$.

A thermodynamic property of the montmorillonite-water system is $\bar{h}_w - h_w°$, the relative partial specific enthalpy of the water. To determine this property, samples of the Na-montmorillonite were brought to different $H_2O$ contents by methods 1, 2, and 3, and then Q, the heat of immersion, i.e., the heat released by immersing the sample in water, was measured calorimetrically at 25°C as described by Oliphant and Low (1982). Because

$$\bar{h}_w - h_w° = dQ/d(m_w/m_c), \qquad (1)$$

values of $\bar{h}_w - h_w°$ were subsequently determined at several values of $m_w/m_c$ by plotting Q against $m_w/m_c$ and taking the slopes of the resulting curve at these values of $m_w/m_c$. Slopes were obtained by the method of Swartzendruber and Olson (1963).

## RESULTS

### Adsorption and desorption of water

Isotherms for the adsorption and desorption of $H_2O$ on Na-montmorillonite, as obtained by methods 1, 2, and 3, are presented in Figure 1. From this figure, it is evident that the desorption isotherms for V-adsorbed and L-adsorbed $H_2O$ coincided, but were different from the adsorption isotherm for V-adsorbed $H_2O$. Hence, the amount of $H_2O$ adsorbed at any $p/p°$ did not depend on the phase, vapor or liquid, from which it was adsorbed, but was different for adsorption than for desorption. The results with $D_2O$ are not presented here, but, as shown in the work of Fu (1985), they were essentially the same as those for $H_2O$.

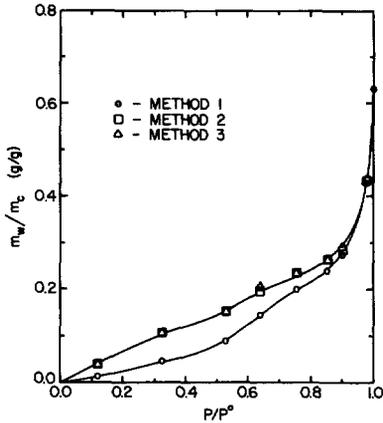If the units of mass are expressed in grams instead

Figure 1. Adsorption and desorption isotherms of Na-montmorillonite at 25°C as affected by different methods of preparing the sample.

of moles, a familiar thermodynamic equation is

$$\bar{g}_w - g_w{}^0 = (RT/M_w)\ln(p/p^\circ), \qquad (2)$$

where $\bar{g}_w - g_w{}^0$ is the relative partial specific free energy of the water, $M_w$ is its molecular weight, $T$ is the absolute temperature, and $R$ is the molar gas constant. Thus, the value of $\bar{g}_w - g_w{}^0$ at any value of $m_w/m_c$ depended on whether that value of $m_w/m_c$ was established by adsorption or desorption, but was the same for V-adsorbed and L-adsorbed water.

## c-axis spacings

Shown in Figure 2 are the 001 diffraction peaks of Na-montmorillonite samples that were brought to equilibrium with $H_2O$ vapor at the specified values of $p/p^\circ$ by methods 1, 2, and 3. Note from this figure that the peaks corresponding to methods 2 and 3 were identical but were narrower and more intense than those corresponding to method 1, especially at low values of $p/p^\circ$. All of the diffraction peaks, however, tended to narrow and intensify as $p/p^\circ$ (and, hence, $m_w/m_c$) increased. The tendency for XRD peaks of montmorillonite to sharpen with increasing $p/p^\circ$ was also observed by Méring and Brindley (1967) and Margheim (1977). It is known (Suquet et al., 1975; Brindley, 1980) that the XRD peak of a phyllosilicate such as montmorillonite narrows and intensifies as the layers of the phyllosilicate become less randomly arranged. But, V-adsorbed and L-adsorbed water had the same effect on the orderliness of the layers. Consequently, the layers were probably less ordered in their arrangement during adsorption than during desorption. The difference in orderliness, however, tended to decrease as the water content increased.

Figure 3 shows curves of c-axis spacing vs. $m_w/m_c$ that were obtained from the data in Figures 1 and 2. Almost identical curves were obtained with $D_2O$ as the adsorbate (Fu, 1985). Apparently, the method of establishing the final water content affected the c-axis spacing only in the transitional region between 12.6 and 15.4 Å. This is the region in which the thickness
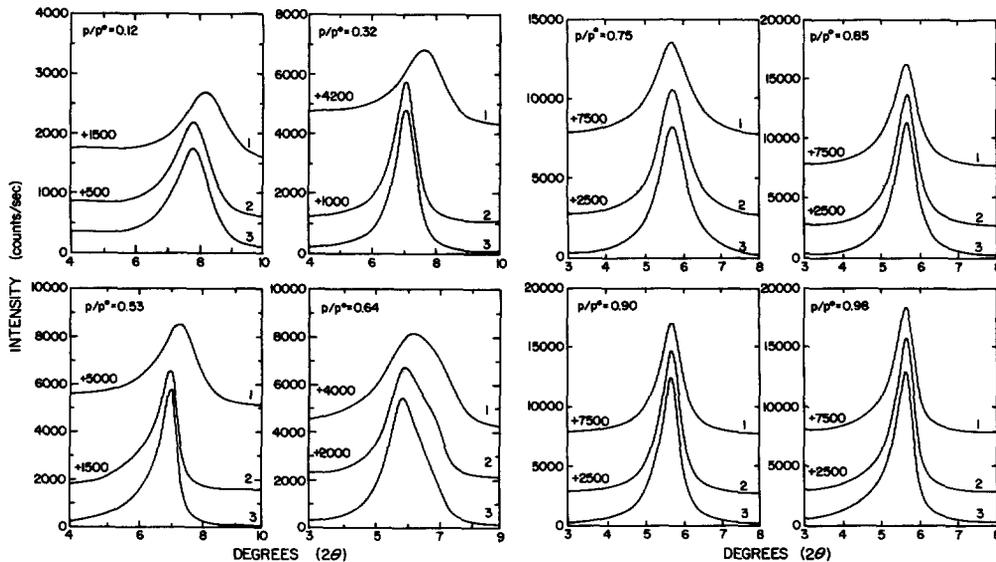


Figure 2. The 001 diffraction peaks of Na-montmorillonite at different values of $p/p^\circ$, the relative humidity (numbers on the left-hand branches of the peaks are the vertical displacements of the peaks in counts per second; numbers on the right-hand branches of the peaks identify the methods by which the samples were prepared). CuK$\alpha$ radiation.
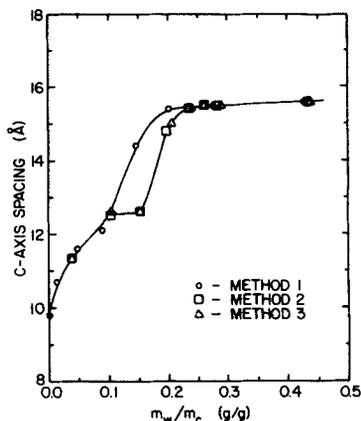
Figure 3. The c-axis spacing of Na-montmorillonite as a function of $m_w/m_c$, the mass ratio of water to montmorillonite, as affected by different methods of preparing the sample. CuKα radiation.



Figure 4. Relation between $\nu$, the O–D stretching frequency, and $m_w/m_c$, the mass ratio of $D_2O$ to Na-montmorillonite, as affected by different methods of preparing the sample.

of the interlayer water changes from one to two molecular diameters or vice versa.

If c-axis spacings are small, an XRD peak can be identified with a discrete c-axis spacing only if this spacing corresponds to the thickness of a unit layer of montmorillonite (~10 Å) plus an integral number of water layers; otherwise, it must be identified with the weighted average of two or more interlayer spacings (Reynolds, 1980). Except for the c-axis spacings of 12.6 and 15.4 Å, all the c-axis spacings reported in Figure 3 must be such averages. This means that, in the regions in which the curves in Figure 3 coincide, the distribution of interlayer distances was independent of the method by which the samples were prepared. As noted above, however, the orderliness of the layers was affected in the same region by the method of preparation. Thus, the orderliness of the layers was apparently affected by factors in addition to the distribution of distances between them, e.g., by their corrugation, bending, folding, rotation, tilting, or translation.

In Figure 2, the XRD patterns labelled 3 were obtained while the samples were being dehydrated the first time, those labelled 1 were obtained while the samples were being rehydrated, and those labelled 2 were obtained while the samples were being dehydrated again. In other words, the XRD patterns corresponding to dehydration were obtained before and after those corresponding to hydration. Yet, the XRD patterns corresponding to dehydration indicated a relatively high degree of orderliness at values of p/p° as low as 0.12 ($m_w/m_c$ = 0.04); those corresponding to hydration indicated a relatively low degree of orderliness to values of p/p° as high as 0.75 ($m_w/m_c$ = 0.2). When the layers were fully hydrated by the adsorption of water vapor at p/p° = 1.0, the value of $m_w/m_c$ was between 0.6 and 0.7. Consequently, disordering of the
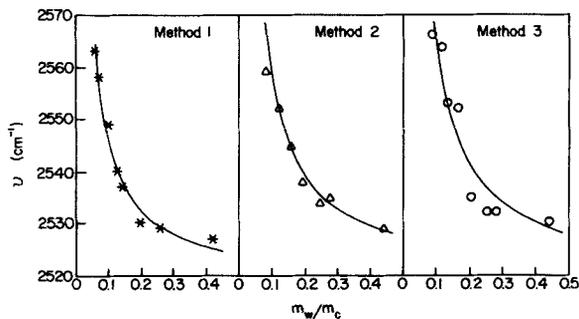
layers must have occurred rapidly during their final stage of dehydration, and ordering of the layers must have occurred gradually after they were partially hydrated.

Reference to Figure 3 shows that, for c-axis spacings between 12.6 and 15.4 Å, the transition from one spacing to the other was monotonous during adsorption but was nearly stepwise during desorption. This means that the layers were distributed between the 12.6-Å state and the 15.4-Å state during adsorption, but existed largely in one state or the other during desorption. A component is more randomly arranged and, accordingly, has a higher entropy if it is distributed between two states than if it exists in only one state. Consequently, in the aforementioned range, the entropy of the layers was probably higher during adsorption than during desorption.

## Frequencies of O–D stretching

Figure 4 illustrates the relations between $\nu$, the O–D stretching frequency, and $m_w/m_c$ for montmorillonite-$D_2O$ samples prepared by methods 1, 2, and 3. Note that, regardless of the method of preparation, $\nu$ increased with decreasing $m_w/m_c$. As mentioned above,
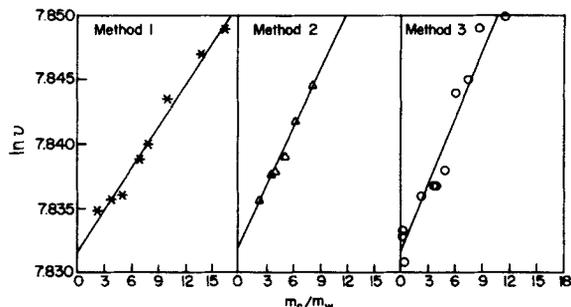


Figure 5. Relation between the logarithm of $\nu$, the O–D stretching frequency, and $m_c/m_w$, the mass ratio of Na-montmorillonite to $D_2O$, as affected by different methods of preparing the sample.

$\nu$ increases as the length of the hydrogen bond becomes longer. Hence, the hydrogen bonds in the films of adsorbed water became longer as these films became thinner.

In agreement with the work of Low (1979) and Sallé de Chou et al. (1980), Figure 5 shows that

$$\nu = \nu^0 \exp[\beta(m_c/m_w)], \qquad (3)$$

where $\nu^0$ is the frequency of O–D stretching in pure $D_2O$ and $\beta$ is a constant. The values of $\beta$, determined from the slopes of the graphs corresponding to methods 1, 2, and 3, were 0.00108 ± 0.00010, 0.00152 ± 0.00010, and 0.00175 ± 0.00040, respectively. The common value of $\nu^0$, determined from the intercepts of these graphs on the $\ln \nu$ axis, was 2519 ± 0.7 cm$^{-1}$. Observe that the values of $\beta$ for the samples prepared by methods 2 and 3 were within experimental error of each other, whereas, the value of $\beta$ for the samples prepared by method 1 was relatively small. Sallé de Chou et al. (1980) showed that $\beta$ in Eq. (3) increased linearly with A, the specific surface area of the phyllosilicate, and Mulla and Low (1983) and Sun et al. (1986) showed that, for all water properties described by the respective analogues of Eq. (3),

$$\beta = kA, \qquad (4)$$

where k is a constant characteristic of the property. Therefore, in the range of $m_w/m_c$ over which $\nu$ was measured (i.e., 0.05 to 0.45), A was smaller during adsorption than during desorption. Because a change in A can arise only by a change in the fraction of unexpanded or collapsed layers (Odom and Low, 1978), some of the layers must have remained in the unexpanded state during adsorption until $m_w/m_c$ exceeded ~0.45 and then, after expanding at higher values of $m_w/m_c$, did not return to this state until desorption was nearly finished. Recall that the layers had a relatively low degree of orderliness during the initial stages of adsorption and that the orderliness they attained thereafter was retained until the subsequent desorption was almost finished. Therefore, the degree of expansion and the degree of orderliness appear to be related. According to Eq. (4), the ratio of the values of A for adsorption and desorption equals the ratio of the corresponding values of $\beta$. Hence, the value of A during adsorption was about two thirds the value of A during desorption. Probably, this was the reason why the isotherm for adsorption fell below the isotherms for desorption (Figure 1).

By logical deduction,

$$t = m_w/\rho_w m_c A, \qquad (5)$$

in which t is the average thickness of the water films within and between the particles (stacks of layers) and $\rho_w$ is the density of the water. Because the value of A was smaller during adsorption than during desorption at any $m_w/m_c$, the opposite must have been true for t.

If all the water had been in interlayer regions, t would have been correlated with the c-axis spacing because, under this condition, t would equal half the distance between the surfaces of the layers. This, however, was not so. The c-axis spacing was generally the same for adsorption and desorption. The necessary conclusion is that t was enhanced during adsorption by the presence of extra interparticle water. This conclusion is reasonable because the interparticle space is greater in a disordered system than in an ordered one.

Combination of Eqs. (3), (4), and (5) yields

$$\nu = \nu^0 \exp(k/\rho_w t). \qquad (6)$$

In keeping with this equation, $\nu$ was smaller during adsorption than during desorption.

### Heats of immersion

Values of Q, the heat of immersion, are plotted in Figure 6 against the respective values of $(m_w/m_c)_i$, the initial value of $m_w/m_c$, in the range from 0 to 0.63. In another paper, Zhang and Low (1989) extended the data to higher values of $(m_w/m_c)_i$ and showed that, after reaching a negative minimum, Q rose to a positive maximum and then fell gradually to zero. For the present purpose, however, the data in Figure 6 are sufficient.

It is clear from Figure 6 that Q was independent of the method by which $m_w/m_c$ was established. In view of Eq. (1), it necessarily follows that the same was true of $\bar{h}_w - h_w^0$. A graph of $\bar{h}_w - h_w^0$ vs. $m_w/m_c$ is presented in Figure 7. Consequently, the system lost and gained heat reversibly, and, because immersion of the clay did not change the volume of the system appreciably, the loss or gain of heat corresponded to a loss or gain of energy of the same magnitude. Thus, the changes in energy accompanying hydration of the layers, hydration of the exchangeable cations, separation of the layers, relaxation of the crystal structure, etc., were also reversible.

From thermodynamic theory,

$$\bar{g}_w - g_w^0 = (\bar{h}_w - h_w^0) - T(\bar{s}_w - s_w^0), \qquad (7)$$

and

$$S_f - S_i = \int_{(m_w/m_c)_i}^{(m_w/m_c)_f} (\bar{s}_w - s_w^0)d(m_w/m_c), \qquad (8)$$

where $\bar{s}_w - s_w^0$ is the relative partial specific entropy of the water, S is the entropy of the montmorillonite-water system per gram of clay, and the subscripts i and f denote the initial and final states, respectively. Recall that S is a measure of the randomness or disorder of a system and that $\bar{s}_w = (\partial S/\partial m_w)_{m_c,T,P}$, where P is the pressure. Eq. (7) and the data in Figures 1 and 7 were used to obtain Figure 8. It is clear from the latter figure that $\bar{s}_w - s_w^0$ was the same for V-adsorbed and L-adsorbed water but, if $m_w/m_c < 0.25$, $\bar{s}_w - s_w^0$ was
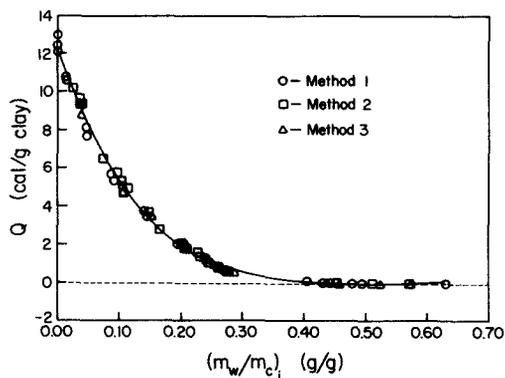
Figure 6.   Relation between heat of immersion, Q, of Na-montmorillonite at 25°C and initial mass ratio of water to montmorillonite, $(m_w/m_c)_i$, as affected by different methods of preparing the sample.



Figure 8.   Relation between relative partial specific entropy, $\bar{s}_w - s_w^0$, of the water adsorbed on Na-montmorillonite at 25°C and mass ratio of water to montmorillonite, $m_w/m_c$, as affected by different methods of preparing the sample.

more negative during adsorption than during desorption.

By using the data in Figure 8, Eq. (8) was integrated graphically to obtain Figure 9. In the latter figure, the $\Delta S$ values on the adsorption curve represent the entropy change that occurred per gram of clay if the given value of $m_w/m_c$ was established by transferring water from pure bulk water to the dry clay; whereas, the values of $\Delta S$ on the desorption curve represent the entropy change that occurred per gram of clay if the given value of $m_w/m_c$ was established by transferring enough water from pure bulk water to the *dry* clay to make $m_w/m_c = 0.65$ and then transferring enough water in the reverse direction to achieve the given value of $m_w/m_c$. Zhang (1985) obtained results identical to those in Figure 9 when he treated our adsorption data by the method of Jura and Hill (1952). Evidently, $\Delta S$ was reversible above, but not below, an $m_w/m_c$ of 0.25. As shown in Figure 3, the clay layers were regularly stratified with two molecular layers of water between them

when $m_w/m_c$ was greater than 0.25. Therefore, the orderliness gained by the interstratified system during adsorption was apparently only partly lost during desorption. This does not mean, however, that the value of S was governed solely by the arrangement of the layers. The arrangement of the interlayer water, which was coupled to the arrangement of the layers, must also have contributed to S.

## DISCUSSION

We have shown that methods 2 and 3 yielded the same results and, hence, that there is no difference between V-adsorbed water and L-adsorbed water. On the other hand, because method 1 yielded different results than methods 2 and 3, adsorption apparently brought the system to a different state than desorption. In other words, hysteresis occurred. Several explanations have been given for the phenomenon of hysteresis, but, as noted by Everett (1967), they do not apply to clay and other materials that swell. In such materials,
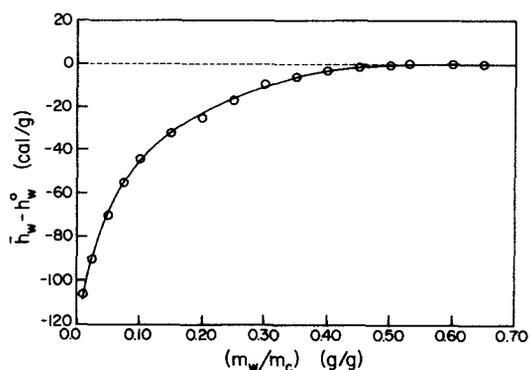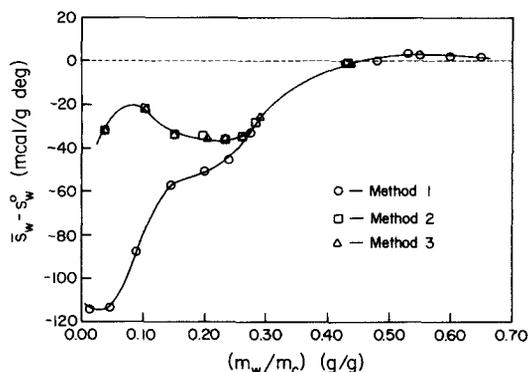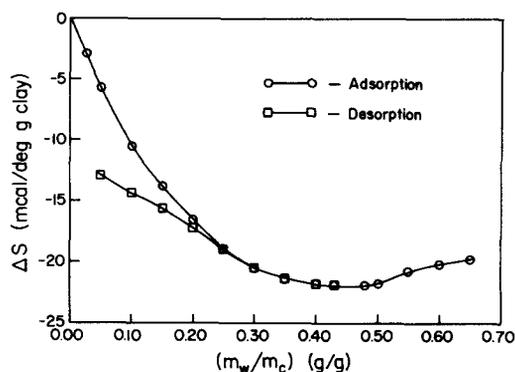


Figure 7.   Relation between relative partial specific enthalpy, $\bar{h}_w - h_w^0$, of water adsorbed on Na-montmorillonite at 25°C and the mass ratio of water to montmorillonite, $m_w/m_c$, as affected by different methods of preparing the sample.



Figure 9.   Relation between change in entropy, $\Delta S$, and mass ratio of water to montmorillonite, $m_w/m_c$, during hydration and dehydration of Na-montmorillonite at 25°C.

hysteresis is believed to be due to irreversible changes that occur in the structure of the material while the adsorbate is being adsorbed. We subscribe to this belief and, based on the results described above, give the following detailed account of what we think happens for montmorillonite.

In a dry montmorillonite, the silicate tetrahedra in the tetrahedral sheet are rotated alternately clockwise and counterclockwise in order to articulate with the alumina octahedra in the octahedral sheet (Radoslovich and Norrish, 1962) and are coordinated with the exchangeable cations occupying the ditrigonal cavities formed by the surface oxygens (Lahav and Bresler, 1973). These cations electrostrict the surrounding structure, and its $b$ dimension therefore decreases as the crystallographic radius of the exchangeable cation decreases (Leonard and Weed, 1967; Ravina and Low, 1977). Probably, the amount of strain energy stored in the structure is increased accordingly. Rotation of the silicate tetrahedra causes the surface network of oxygens to assume ditrigonal symmetry. This kind of symmetry does not allow the layers to fit together in any periodic or regular way, and they rotate, translate, etc., to achieve the best fit possible. Hence, their arrangement is turbostratic. In addition, they are probably not all oriented alike and some of them are likely to be bent or folded over each other. Under such conditions, the degree of disorder is relatively high, and the XRD peaks are correspondingly broad.

If the dry layers are exposed to water vapor, water molecules penetrate the interlayer space (e.g., Mooney et al., 1952; Glaeser and Méring, 1968; Margheim, 1977) and hydrate most of the layer surfaces and exchangeable cations (Rios and Vivaldi, 1950; Odom and Low, 1983; Sposito and Prost, 1982). In the process, the exchangeable cations move out of the ditrigonal cavities (Sposito et al., 1983), their electrostrictive influence on the surrounding structure is reduced, and the structure relaxes. Relaxation of the structure is indicated by an increase in the $b$ dimension (Ravina and Low, 1977; Margheim, 1977). Some of the energy released in the hydration of the surfaces and cations and in the relaxation of the mineral structure is utilized to remove the cations from the ditrigonal cavities and to separate the layers against the prevailing attractive forces, but most of it is lost as heat. Hence, Q has finite positive values that decrease with increasing $m_w/m_c$. During the initial stages of hydration, the water molecules must depart from their normal tetrahedral arrangement so that they can coordinate simultaneously with the surface oxygens of the layers and the exchangeable cations. In effect, they link the opposing surfaces together through the mediation of these cations (Farmer and Russell, 1971; Suquet et al., 1975). More strain exists in the resulting arrangement than in the arrangement characteristic of bulk water, and, accordingly, S and $v$ are relatively high. As the interlayer

water continues to accrue, the layers rotate, translate, etc. in response to the stress imposed on them by the water, and the accompanying loss of strain energy contributes to Q. Also, the increase in orderliness of the layers and interlayer water sharpens the 001 XRD peak and reduce S and $v$. By the time $m_w/m_c$ has reached a value of $\sim$0.45, the system has reached its most ordered state and S is at a minimum. Moreover, the value of $v$ is close to that of pure bulk water.

When desorption follows adsorption, all of the processes described above occur in the opposite direction and energy is regained reversibly. The degree of order achieved during adsorption, however, is not entirely lost until desorption is essentially finished. Thus, hysteresis occurs because the orderliness of the system is not reversible, and any property that depends on orderliness is hysteretic.

## ACKNOWLEDGMENT

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