

WATER VAPOR ISOTHERMS AND HEAT OF IMMERSION OF Na/Ca-MONTMORILLONITE SYSTEMS—I: HOMOIONIC CLAY

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Abstract—Adsorption isotherms for water vapor, *c*-spacing and heat of immersion in water of Na- and Ca-montmorillonite were measured at 25°C at various r.h. The amount of water adsorbed as a function of the r.h. increased gradually, whereas the *c*-spacing increased, and the heat of immersion (per mole of adsorbed water) decreased in steps. There was good agreement between the calorimetric data, the heat calculated from the isotherms by use of BET equation, and the calculations from the ion-dipole model. A model is presented to describe the hydration of sodium and calcium montmorillonite.

INTRODUCTION

The adsorption of water molecules on clays under controlled vapor pressure, and the heat of immersion, have been studied by a number of workers (Hendricks *et al.*, 1940; Zettlemayer *et al.*, 1955; Mooney *et al.*, 1952; Fripiat *et al.*, 1965; Kijne, 1969). However, very few investigated sodium and calcium montmorillonite in pure and mixed systems in detail, and none of them simultaneously measured the adsorption isotherms, *c*-spacing and heat of immersion on the same ionic clay. The Na- and Ca-montmorillonite systems deserve detailed examination as they are so different from each other. Sodium platelets are completely separated when immersed in distilled water, and the distance between the platelets is determined by the diffuse double layer forces. Conversely, X-ray diffraction data on calcium montmorillonite in distilled water (Blackmore and Miller, 1961; Norrish and Quirk, 1954) indicate that Ca-montmorillonite exists in packets consisting of 3–9 platelets, with a film of water 4.5 Å thick on each internal surface.

Three types of clay-water interactions have been described to account for the expansion in the *c*-direction; (1) hydration of the interlayer cations, (2) hydration of the exposed clay surfaces and (3) an osmotic effect. Hydration of the cations and of the exposed clay surfaces occurs at low water contents, whereas the osmotic phenomenon is more effective at high water content. The relative importance of each of the first two interactions is debatable; Nagelschmidt (1936) and Barshad (1955) suggested that during the initial adsorption of water on montmorillonite, the water molecules are adsorbed on the outer surfaces, whereas Marshall (1936) and Mering (1946) maintained that a uniform hydration of all exchange-

able cations is maintained first. Another model which compromises between the above two extreme approaches was proposed by Hendricks *et al.* (1940). They suggested that in low water contents the Ca²⁺ ions are hydrated first, whereas in Na-clay the cations are not and the initial adsorption of water molecules is on the external surfaces. Quite likely the water molecules forming the first hydration shell around the adsorbed cations have a different energetic level than that of the water molecules residing between the hydration ions.

In order to study these relations the amount of water adsorbed, the *c*-spacing and the heat of immersion at various r.h. and water contents were determined simultaneously for the same batch of clay. From the heat of immersion data it was possible to obtain information on the intensity of the interaction between the water molecules and the sites and thus to determine the sites of water adsorption.

It should be emphasized that the interlayer adsorption process is essentially different from the adsorption on external surfaces. In the dry state, there is an electrostatic attraction between the negative clay platelets and the exchangeable cations located between the platelets and van der Waals forces of attraction between the clay platelets. During the adsorption process, the adsorption energy of the water is the driving force for parting the clay platelets against these two forces of attraction. Therefore the thermodynamic quantities derived from the experimental observation reflect the net effect of the hydration energy and the platelet's attraction energies as well as the net effect of changes in the water phase, lattice geometry and position of the cations.

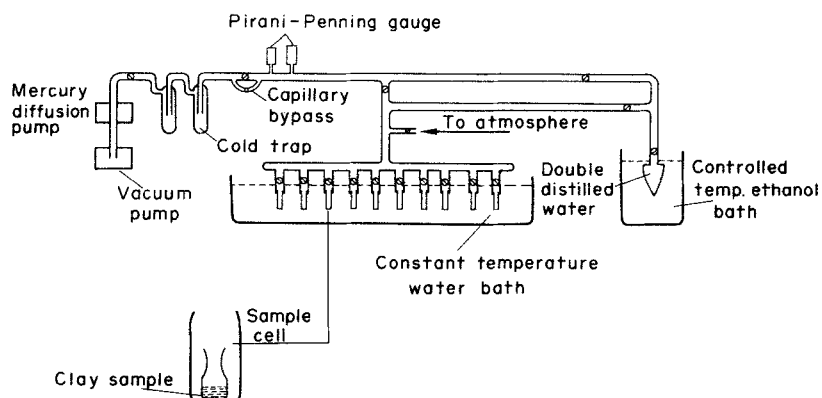


Fig. 1. Schematic diagram of water sorption apparatus.

EXPERIMENTAL METHODS

Clay preparation

The clay fraction of Wyoming bentonite (API No. 25) was obtained by allowing larger fractions to settle out of a suspension and then decanting the suspension. *M*-clay ($M = \text{Na}^+$ or Ca^{2+}) was prepared by saturating the colloidal fraction with normal MCl solutions. This treatment was repeated three times. Then, the clay was washed with distilled water and separated in a high-speed centrifuge until the equilibrium solution was free of chlorides. Chloride was presumed to be absent when the supernatant liquid tested negative with AgNO_3 . The salt-free clay was freeze-dried and stored in a desiccator over P_2O_5 . The ion exchange capacity of this clay is 0.90 mequiv./g dry clay.

Adsorption isotherm determinations

Two methods were used to determine the adsorption isotherms in order to know whether a real equilibrium was obtained. In the first method the clay samples were kept in desiccators over H_2SO_4 solutions of different r.h. for several weeks until an equilibrium was maintained. A schematic presentation of the second method is shown in Fig. 1. The clay samples were kept in a constant temperature water bath at $25^\circ\text{C} \pm 0.1$, and were connected to a vessel containing double-distilled water free of adsorbed gases, immersed in an ethanol bath maintained at various temperatures corresponding to the r.h. The temperature fluctuations in the ethanol bath were less than 0.02°C .

The amount of adsorbed water in both systems was obtained by weighing, and expressed in mg of water/g clay dried at 105°C for 24 hr. In a preliminary experiment it was found that during the first minute a clay dried in a vacuum of 10^{-5} mm Hg, was exposed to air with a relative humidity of 75 per cent, 0.1 mg of water was adsorbed by a Ca-clay and 0.08 mg on a Na-clay. In our experiment the elapsed time between opening the system until weighing was less

than half a minute, so that the change in weight of the clay during weighing was small and could be neglected.

De-gassing the clay samples at 1×10^{-5} mm Hg and 25°C for 1 week was as efficient for drying the clay as heating at 105°C . Conversely, drying over P_2O_5 was not so efficient in replacing the adsorbed water. Thus, a significant error may exist in the isotherms reported by those who used clay dried over P_2O_5 . In these experiments the Na- and Ca-clay dried over P_2O_5 contained 0.6 and 3.0 per cent water, respectively, compared with oven-dried clay.

Blank determinations with an empty sample tube showed that the glass adsorbed a negligible quantity of water (<0.1 mg). The samples in the high-vacuum method were equilibrated with water vapor at increasing and decreasing vapor pressures. Hysteresis phenomena in the adsorption-desorption cycle were observed for both Na- and Ca-montmorillonite (Fig. 2).

Calorimetric determinations

The heat of immersion of the clays equilibrated with the various relative humidities was measured in a Guild* solution calorimeter. This calorimeter is similar to the one described by Arnett *et al.* (1965). The container was a 200 ml cylindrical Dewar flask enclosed in a PVC jacket fitted with a Plexiglas-Teflon cup which could be fixed to the jacket by bolts. The heat-sensing element was a 5000Ω (nominal) Veco thermistor† having a temperature coefficient of 4 per cent $^\circ\text{C}$.

The heating element had a constant resistance at 25°C . The heat of stirring and the constant heat leakage to or from the outside caused the base line to drift steadily. This drift was corrected with a base line compensator. A proportional temperature controller was used to improve the adiabatic conditions by regulating the outer water temperature to follow the water temperature changes in the Dewar flask caused by the stirring and reaction process.

The samples were placed in a cylindrical stainless-steel cell with two Teflon stoppers. These stoppers could be opened by pushing an ebonite rod from the

* Guild Co., U.S.A.

† No. 35A3, Victory Engineering Corporation, U.S.A.

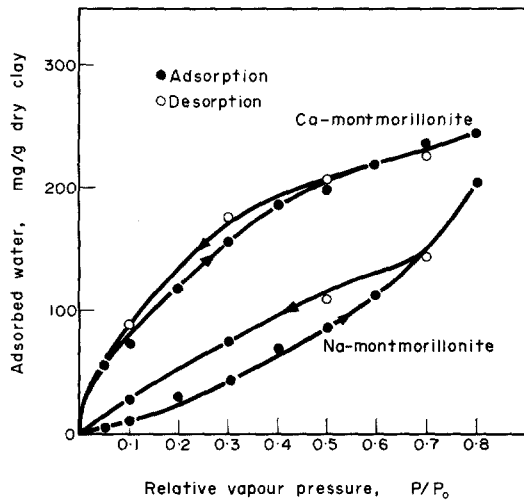


Fig. 2. Adsorption-desorption isotherms on Na- and Ca-montmorillonite.

outside. The heat generated in opening the cell was considered in the calculations. Temperature changes in the Dewar flask were recorded with a Sargent recorder Model SRG (1 mv full scale).

The calorimeter was calibrated by introducing a known amount of electrical energy and observing the resultant temperature rise. The reliability of the calorimeter was checked by measuring the heat of solution of crystalline KCl. Good agreement was obtained with data in the literature (Somsen *et al.*, 1963). Determinations were made on at least two samples.

X-ray determinations

The clay suspensions were sucked through ceramic tiles in order to obtain a good orientation of the particles for X-ray studies. The tiles with the film of clay were placed in a desiccator at various r.h. until equilibrium was reached. X-ray powder diffraction was measured on a Seifert X-ray unit with automatic recording by a diffractometer (model MZ1). The diffraction of nickel-filtered copper K_{α} radiation at a scanning speed of $0.5^{\circ} 2\theta/\text{min}$ was recorded from $2\theta = 3^{\circ}$ to $2\theta = 13^{\circ}$.

RESULTS AND DISCUSSION

Hysteresis phenomenon

Adsorption-desorption isotherms as obtained in the high-vacuum method are presented in Fig. 2. It is evident that the adsorption and desorption curves are not the same and that hysteresis took place. The desorption branch of the hysteresis loop has more vapor sorbed at a given vapor pressure than has the adsorption branch, up to 0.6 and 0.7 r.h. for the calcium and sodium curves, respectively (Fig. 2). Above this vapor pressure the desorption and adsorption curves coincide. It is evident that the hysteresis behavior is more pronounced for the Na-clay than for the Ca-clay. The hysteresis behavior of montmorillonite may arise from one or more of the following factors;

(a) capillary condensation, (b) the change in rigidity of the water adsorption on the exchangeable ions between the platelets and (c) the variety of geometric situations in which filling and emptying paths are different. The capillary and geometric factors are more pronounced in the desorption curves and have no relevance to the cation-water or surface-water interactions. Thus, only the adsorption branch of the isotherms was analyzed.

Adsorption isotherms and X-ray data

The isotherm of water vapor adsorption by Na- and Ca-montmorillonite at $25 \pm 0.5^{\circ}\text{C}$, in both methods, together with the *c*-spacing of the same clay at the same r.h. and with data obtained by Mooney *et al.* (1952), Zettlemayer *et al.* (1955) and Fripiat *et al.* (1965), are presented in Fig. 3. The amount of water adsorbed by the Ca-clay is greater than that by the Na-clay up to a r.h. of 0.85. At this value the two isotherms cross, and at higher r.h. the amount of water adsorbed by the Na-clay is greater than that by the Ca-clay. This indicates that in the lower range of r.h. (up to 0.85), the interaction forces between Ca-clay and water are greater than those between Na-clay and water. The amount of water adsorbed on Na-montmorillonite exceeds that on Ca-clay at high r.h. because of limited swelling in the Ca-system. The same conclusion may be derived from consideration of the general shape of the isotherms in the 0-0.85 r.h. interval. The Ca-isotherm is concave downward while the curve of water adsorption by Na-montmorillonite is concave upward. Analysis of these shapes according to the BET theory (see later) indicates that in the Ca-system the energy of interaction between the first mono-layer of water molecules adsorbed and the active surfaces (E_1) is greater than the energy of condensation of the subsequent layers (E_L). In Na-montmorillonite the difference between these two energy terms is less, indicating that the hydration

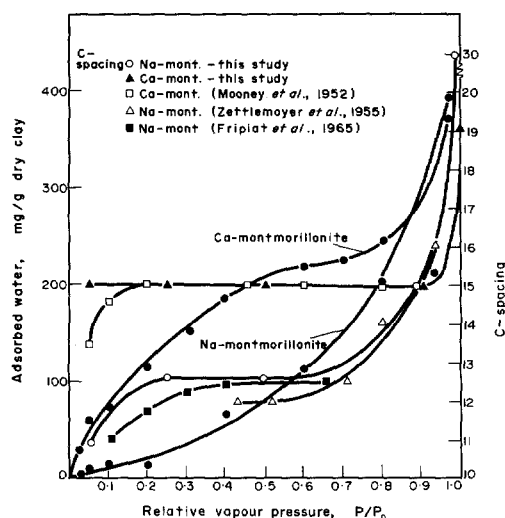


Fig. 3. Adsorption isotherms (the closed dots) and *c*-spacing of Na- and Ca-montmorillonite.

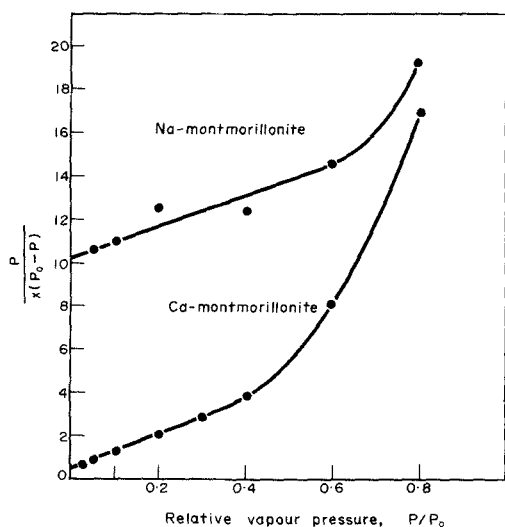


Fig. 4. BET curves of the adsorption isotherms.

forces in Na-montmorillonite are less than those in Ca-montmorillonite.

In comparing the isotherms with *c*-spacing data it is evident that although the weight of the water adsorbed increases continuously with a continuous increase in r.h., the *c*-spacing changes in steps. This is in contrast to the observation made by Van Olphen (1965) who found for the adsorption of water vapors on Na-vermiculite that both the weight of water adsorbed and the *c*-spacing increased in steps. Moreover, in the wide range of relative humidities in which water molecules are adsorbed on Ca-montmorillonite, the *c*-spacing obtained by X-ray remains constant at 15 Å (Fig. 3). This suggests that the two layers of water form immediately upon the initial hydration of Ca-montmorillonite without passing through the one-layer stage, and as the r.h. increases, more water molecules penetrate the interlayer to complete the two monolayers of water molecules.

The Langmuir theory assumes that gases, in being adsorbed by a solid surface, form only a monolayer of adsorbate. According to the BET theory, adsorption involves the formation of many molecular layers on the surface. The BET equation may be written as follows:

$$\frac{P}{X(P_0 - P)} = \frac{1}{X_m C} + \frac{C - 1}{X_m C} \cdot \frac{P}{P_0} \quad (1)$$

where *X* is the amount of water adsorbed in grams

Table 1. The BET parameters and the heat of water adsorption on Na⁺ and Ca²⁺ montmorillonite calculated from them at 25°C

Adsorbed ion	<i>X_m</i> mg H ₂ O/g clay	<i>N</i> water molecules per ion	<i>C</i>	<i>E₁</i> - <i>E_L</i> kcal/mole
Na	58	3.6	1.7	0.34
Ca	114	14.5	14.3	1.58

per gram of adsorbent at pressure *P*, and temperature *T*, *P₀* is the saturated vapor pressure at the same temperature, *X_m* is the quantity of adsorbate adsorbed when the adsorbent is covered with a monolayer, and *C* is a constant at any given temperature, and approximately equals

$$C = \text{EXP}(E_1 - E_L/RT) \quad (2)$$

where

E₁ is the heat of adsorption of the first layer, *E_L* is the heat of liquifaction of the gas (= 10480 cal/mole for water at 25°C).

R is the molar gas constant,

and

T is the absolute temperature.

According to equation (1), a plot of *P*/*X*(*P₀* - *P*) vs *P*/*P₀* should give a straight line with the slope given by *C* - 1/*CX_m* and the intercept by 1/*CX_m*. The application of this equation to our experimental data is presented in Fig. 4.

It is evident that the BET plot does yield linear relations in the 0-0.6 and 0-0.4 r.h. regions for Na- and Ca-montmorillonite, respectively. From the slopes and intercepts of these lines, the mass of water/clay required to form a monomolecular layer (*X_m*), and the heat of adsorption (*E₁* - *E_L*), were calculated and are given in Table 1. These values are in good agreement with those reported by Quirk (1955). A further discussion of these values is presented together with the discussion of the experimental results obtained calorimetrically.

Calorimetric measurements

The heat of immersion of Na- and Ca-montmorillonite equilibrated with different amounts of water in the adsorbed phase, is presented in Fig. 5. The data show that the heat evolved/g clay when dry Ca-

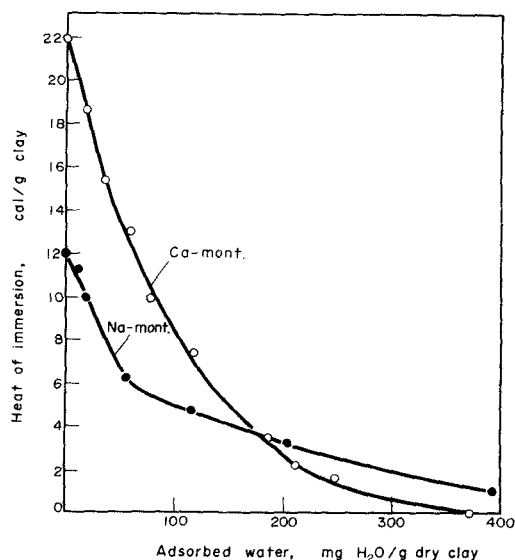


Fig. 5. Heat of immersion of Na- and Ca-montmorillonite (cal/g) equilibrated with various amounts of adsorbed water.

montmorillonite is immersed in distilled water (22 cal/g) is about twice as much as the corresponding value for Na-clay (12 cal/g). These experimental values are in good agreement with the values reported by Anderson and Sposito (1964), Slabaugh (1955) and Kijne (1969) for the same montmorillonite. As expected, less heat is evolved when a partially saturated clay sample is immersed in distilled water (Fig. 5). When wet Na- and Ca-clay samples (e.g. in equilibrium with r.h. of 0.97) are immersed in distilled water (these clay samples contain 392 and 372 mg of H₂O/g clay for Na- and Ca-montmorillonite, respectively) the heat evolved is 1.0 cal/g and zero for Na- and Ca-montmorillonite, respectively. The heat evolved when wet Na-clay is immersed in distilled water probably is due to the exothermic hydrolysis and decomposition of the Na-montmorillonite in water suspensions (Kamil and Shainberg, 1968; Brown and Miller, 1971). Since the extent of hydrolysis for Ca-montmorillonite is much less than that for Na-clay, the heat evolved when wet Ca-clay is immersed in distilled water is negligible.

The heat of adsorption of water/mole water) on Na- and Ca-montmorillonite has been calculated from equation (3) and is presented in Fig. 6.

$$E_1 = \frac{U_{N_2} - U_{N_1}}{\Delta N} \quad (3)$$

where U_{N_1} and U_{N_2} are the heat of immersion of clays adsorbed with N_1 and N_2 moles of water, respectively, and ΔN is equal to $(N_2 - N_1)$.

It is evident from Fig. 6 that the heat evolved/mole adsorbed water for Na-montmorillonite follows completely different curves from that of Ca-montmorillonite. For Na-montmorillonite energetically there are two kinds of adsorbed water:

(1) The first three m-mole of water molecules adsorbed on one g clay (which corresponds to about 3 m-mole of H₂O/m-equiv. of Na-ions) liberate about 1.8 kcal/mole upon passing from bulk water to the adsorbed phase.

(2) The subsequent adsorbed water molecules liberate only 0.4 kcal/mole H₂O upon being adsorbed on the clay.

Conversely, when considering the heat of adsorption curve for Ca-montmorillonite, one cannot distinguish simply between two kinds of adsorbed water. For the first 2 m-mole of water adsorbed on one g/clay (which correspond to about 4 m-mole of water per m-mole of Ca²⁺ ions), the heat evolved is 3.3 kcal/mole adsorbed water. The heat evolved then decreases to 2.5 kcal/mole adsorbed water, for the third m-mole of H₂O/g clay (which correspond to the 5th and 6th molecules of H₂O per Ca²⁺ ion adsorbed on the clay). Next, there is a continuous decrease in the heat evolved, until no heat is evolved when vapor saturated Ca-montmorillonite is immersed in distilled water.

These two types of curves, together with the adsorption isotherms and the *c*-spacing data, enable us to suggest the mechanism and sites of water

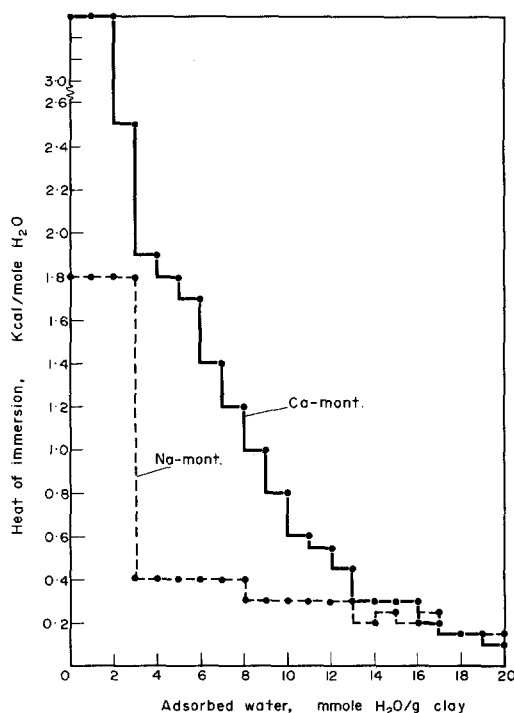


Fig. 6. Amount of heat released per m-mole of water adsorbed on Na- and Ca-montmorillonite.

adsorbed on montmorillonite clay. This is discussed separately for Na- and Ca-montmorillonite.

Na-montmorillonite systems

The *c*-spacing of a dry montmorillonite clay is 9.6 Å. The *c*-spacing of one-layer hydrate (at r.h. up to 0.6) is 12.6 Å. This gap between the platelets is large enough to accommodate one monolayer of water molecules. The volume of interlayer water in the complete one-layer hydrate is $760/2 \cdot 10^4 \cdot 3 \cdot 10^{-8} = 0.114$ ml, which corresponds to 114 mg of water (=6.33 m-mole of H₂O) per g/clay, or seven molecules of water/sodium ion for these calculations. It was assumed that the specific surface area of montmorillonite is 760 m²/g and the cation exchange capacity is 0.9 m-equiv./g). However, if we consider the parameters derived from the adsorption isotherms at the r.h. range up to 0.6 (Table 1), the weight of water adsorbed in the first BET monolayer is 58 mg/g clay. A similar value is obtained when considering the calorimetric data. The heat of adsorption for the initial 54 mg of water (which corresponds to 3 m-mole of H₂O/g clay or 3.3 water molecules/sodium ion) is constant at a value of 1.8 kcal/mole water. Thus, the first 3 m-mole of H₂O/g clay are energetically equal and occupy the same sites on the clay. In the dry state the cations are placed in the hexagonal cavities in the surface or in close packing with the oxygens of the silicon tetrahedra. Upon introducing one layer of water molecules, the first three water molecules are adsorbed at the Na⁺ ions. Thus, the adsorbed ions will be in octahedral coordination

with three oxygens of the surface and three water molecules forming the monolayer of water molecules.

Considering again the adsorption isotherm of Na-montmorillonite (Fig. 3), the *c*-spacing reaches a constant value of 12.6 Å at a r.h. of about 0.3. At this r.h. the amount of water adsorbed is 34 mg/g clay, which corresponds to two water molecules/ion. Two possibilities exist for the position of those water molecules; only 2/3 of the exchangeable ions are hydrated with three water molecules per ion, and all the Na⁺ ions are hydrated, but with only two water molecules per ion.

Irrespective of the real situation (which is probably in between the above two extreme possibilities) it is clear that introducing only 2/3 of the amount of water needed to form a complete monolayer (X_m) is enough to overcome the electrostatic attraction forces between the clay platelets.

The *c*-spacing does not change with increase in r.h., until a r.h. value of about 0.6 is reached. The amount of water adsorbed at r.h. 0.6 is 114 mg/g clay. This value coincides with the theoretical weight of the complete monolayer. This indicates that a monolayer of water molecules is first completed before a second layer is formed.

Between r.h. 0.3 (with 34 mg H₂O adsorbed/g clay) and r.h. 0.6 (with 114 mg H₂O adsorbed/g clay), the amount of water adsorbed increases continuously with increasing r.h. without any change in the *c*-spacing. The energy of the water adsorbed at this r.h. range is not uniform. The energy evolved when the third m-mole of H₂O is being adsorbed on the clay is about the same as the energy evolved upon wetting by the first two m-mole of H₂O (1.8 kcal/mole H₂O). Thus, this m-mole of water occupies a site equivalent in energetic status to the two previous m-moles of water. The energetic level of the 4th to 7th m-mole of water adsorbed/g clay, decreases markedly to a constant value of 0.4 kcal/mole H₂O. These water molecules fill the gap between the hydrated exchangeable ions. They either complete the second sheet of water adsorbed on the cation, or are adsorbed directly to the free oxygen surfaces of the clay.

Between r.h. 0.6 and 0.9, the second layer of water molecules is formed. The heat of adsorption of these water molecules is uniform at 0.3 kcal/mole H₂O. At r.h. above 0.9, the *c*-spacing increases to 18.9 Å and more, and the amount of water adsorbed is not related to the weight of the monolayer formed. For example, at r.h. of 0.9, the amount of water adsorbed is 300 mg/g clay, whereas the *c*-spacing is only 15.0 Å, which indicates that only two monolayers of water molecules are in between the platelets. The weight of water in two completed monolayers is 228 mg/g. Thus, the excess of water (72 mg/g) is adsorbed on the outer surfaces by condensation.

The above described model for water adsorption on Na-montmorillonite is different from that suggested by Van Olphen (1965) for Na-vermiculite. He suggested (based on calorimetric and adsorption isotherm data) that for Na-vermiculite the integral heat

of sorption per mole of water was constant during the formation of each layer of water, and that the heat of sorption for the first layer per mole of water was about twice that for the second layer. We found that for Na-montmorillonite the heat of sorption was not constant during the formation of each monolayer. A possible reason for this difference is the high charge density of vermiculite, which is about twice that of montmorillonite.

Ca-montmorillonite systems

The amount of water adsorbed on Ca-montmorillonite at r.h. of 0.05 is 57 mg water/g clay, or seven water molecules/Ca²⁺ ion. At this r.h. the *c*-spacing is already 15 Å. This indicates that a space able to accommodate two monolayers of water molecules (namely, 228 mg H₂O/g clay or 28 water molecules/Ca²⁺ ion), was already available at this relatively low water content. At a similar water content for Na-montmorillonite, only an incomplete monolayer of water is formed. This effect can be explained by the heat of adsorption of these water molecules. The heat evolved/one mole of adsorbed water, as calculated from the calorimetric measurements (Fig. 6), is 3.3 kcal/mole H₂O for the first two m-mole of H₂O adsorbed on 1 gram of clay (which corresponds to 4.5 molecules/exchangeable Ca²⁺), and it decreases to 2.5 kcal/mole for the third m-mole of water adsorbed on the clay. From the 4th m-mole of water and on, the heat decreases continuously to 1.9, 1.8, 1.7, 1.4 kcal/mole, etc. Thus, the heat of sorption of the first three m-mole of water adsorbed on Ca-montmorillonite (which corresponds to seven water molecules/Ca²⁺ ion) is quite high and this might explain why these water molecules are able to push apart the clay platelets to a *c*-spacing of 15.0 Å. In this expanded state, the Ca²⁺ ions are coordinated with 6–8 water molecules, as is expected theoretically from the radius ratio principle.

As the r.h. increases above 0.05, the amount of water adsorbed increased continuously up to a r.h. of about 0.6. At about this point there is an inflection point in the curve, with a reduction in the rate of increase in the sorbed water with an increase in the r.h. The amount of water adsorbed at r.h. 0.6 is 220 mg/g clay, which corresponds roughly to the amount of water in two complete monolayers of water. Thus it seems that, because there is no room for more water molecules, less water is being adsorbed. As the r.h. increases above 0.8, the *c*-spacing is still constant at a value of 15.0 Å, but the rate of water adsorption increases again. It seems that at a r.h. above 0.8, water molecules condense on the outer surfaces, thus increasing sorbed water without a change in *c*-spacing. The same phenomenon was observed for Na-montmorillonite at a r.h. above 0.8.

Both BET analysis of the adsorption isotherms and the calorimetric data are not conclusive about the sites of the adsorbed water molecules beyond the first 6–8 which form the octahedral or cubohedral structure around exchangeable Ca²⁺ ions. Hill (1946) sug-

gests that, according to the BET analysis, a C -value (equation 2) of 10 indicated the formation of a multilayer of adsorbate before the first layer is complete. For the substantial completion of the first layer before another layer is begun, a C -value of 100 or more is required. We obtained a C -value of 14.5 which suggests the formation of multilayer of water molecules. The calorimetric data also indicate that the energy level of the consecutive water molecules (beyond the first seven H_2O molecules/ Ca^{2+} ion) decreases gradually and continuously. Thus, it seems that at r.h. of 0.05, the first sheet of water molecules around the Ca^{2+} ions is completed and the c -spacing is already 15 Å. As the r.h. increases, the vacancies between the hydrated ions are continuously filled with water molecules. When the space between the platelets is filled (at r.h. of about 0.6), the adsorption isotherm becomes flat, and only when the r.h. increases above 0.8, condensation of water molecules on the outer surfaces of the tactoids takes place and the adsorption curve becomes concave upward again.

Above r.h. 0.9, the c -spacing increases to a maximum value of 19 Å, and the heat of water adsorption decreases to zero when the liquid water molecules are taken as the standard state (Fig. 5).

Theoretical prediction of the heat of wetting

The heat of adsorption of the first sheath of water molecules around the exchangeable cations were found to be 1.8 and 3.3 kcal/mole of H_2O for Na- and Ca-montmorillonite, respectively. The heat of hydration can also be calculated by equations based on the structural treatment of ion-solvent interaction, proposed by Bernal and Fowler (1933).

The water molecules in the hydration shell lose the energy, E_a , resulting from ion dipole forces which bind the water molecules to the ion, but gain the energy E_w , resulting from the reduced possibilities of hydrogen bonding with other water molecules, as occurs in bulk water. The net change in energy, E_A , may be computed as

$$E_A = E_a + E_w \quad (4)$$

in which

$$E_a = - \frac{N_A \cdot n \cdot Z_i \cdot e \cdot \mu_w}{\epsilon_w (r_i + r_w)^2} \quad (5)$$

where N_A is Avogadro's number, n is the number of water molecules in the first sheath, Z_i is the ion valency, e is the electronic charge, μ_w is the dipole

moment of the water molecule in the liquid phase, r_i and r_w are the ion and water molecule radii, respectively ($r_{\text{Na}^+} = 0.95 \text{ \AA}$, $r_{\text{Ca}^{2+}} = 0.99 \text{ \AA}$, $r_w = 1.4 \text{ \AA}$), and ϵ_w is the dielectric constant of the medium.

For the first layer of molecules surrounding an ion, the dielectric constant is about 5 (Ritson and Hasted, from Robinson and Stokes, 1959). Howel and Licastro (1961) found that the dielectric constant of the clay crystal itself was 5 or 6. An average value of 5 has been used for the dielectric constant in the calculations here. The electric dipole moment, μ , of an isolated water molecule has been accurately determined from measurements of the dielectric constant of water vapor at various temperatures, and has a value of 1.84 D (Sanger *et al.*, 1932). Substituting these numerical values in equation 4 gives the values for E_a presented in Table 2.

The H_2O molecule can participate in four hydrogen bonds, two of them involving the two hydrogens of the molecule and two the lone pairs of electrons of the oxygen and the hydrogens of two neighboring molecules. This tetrahedrally directed bonding is involved in the crystal structure of ice. The water molecule coordinated to an ion can coordinate with only two other molecules instead of four as in the case of bulk water. Cross *et al.* (1937) concluded from an analysis of the Raman spectrum of water that at 25°C about 50 per cent of the hydrogen bonds of H_2O are broken. Thus, the water molecule coordinated with an ion have been bonded to only about one water molecule. The average energy of a hydrogen bond is about 7.5×10^{-21} cal (=4500 cal/mole of hydrogen bonds). This energy is shared by two water molecules, so that the average energy per molecule per bond is about 3.8×10^{-21} cal. As a result of losing the possible association of these two neighbors, the water molecule gains an average energy of about 3.8×10^{-21} cal (i.e. $E_w = 2300$ cal/mole H_2O). This value for E_w is also presented in Table 2.

The main attractive force in this system is the electrostatic interaction between the adsorbed ions and the charge plates. The relationship of the ion to the silicate surface is similar to that of a point charge. The attraction energy, E_r , between an adsorbed ion and the electrostatic charge of the platelet is given by

$$E_r = \frac{q_1 \cdot q_2}{\epsilon r} \quad (6)$$

Table 2. Energy released for the three mmole of water adsorbed on Na- and Ca-montmorillonite (experimental and calculated values at 25°C)

Adsorbed ion	Hydration number	Calculated Values (kcal per mole H_2O)				Experimental values* (kcal per mole H_2O)		
		E_a	E_w	ΔE_r	ΔE_{calc}	1st	2nd	3rd
Na^+	3	- 4.6	+ 2.3	+ 1.1	- 1.2	- 1.8	- 1.8	- 1.8
Ca^{+2}	6	- 8.8	+ 2.3	+ 3.3	- 3.2	- 3.3	- 3.3	- 2.5

* Values correspond to the first three mmole of water adsorbed per gram clay.

where q_1 and q_2 are the charges of the adsorbed ion and the clay, respectively, r is the distance between the adsorbed ion and the negative charge of the plate, and ϵ is the dielectric constant. Thus, the energy required to push the platelets apart (and to increase the distance between the adsorbed (hydrated) ion and the clay surface) is

$$\Delta E_r = E_{r_1} - E_{r_2} = \frac{q_1 q_2}{\epsilon} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \quad (7)$$

where r_1 the distance between the adsorbed ion and the plane of negative charge in the dry clay is $9.6/2 = 4.8 \text{ \AA}$, and r_2 for c -spacing of 12.6 and 15 \AA are 6.3 and 7.5 \AA , respectively. These energy terms are also presented in Table 2.

The net energy change in the hydration process of adsorbed ions on clays is given by

$$\Delta E = E_a + E_w + \Delta E_r \quad (8)$$

and is presented in Table 2.

It is evident that reasonable agreement is obtained between the calculated values and the experimental results for Na- and Ca-montmorillonite.

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