

## ADSORPTION OF WATER BY HOMOIONIC EXCHANGE FORMS OF WYOMING MONTMORILLONITE (SWy-1)

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**Abstract**—Adsorption isotherms for water on homoionic (Ca<sup>2+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) exchanged forms of Crook County, Wyoming, montmorillonite (CMS Source Clay SWy-1) were measured between 25° and 70°C using a vacuum microbalance having automated control of water vapor pressure. From these adsorption data, integral enthalpies and entropies of adsorption were calculated. Both quantities were negative, but decreased in magnitude with increasing amounts of adsorbed water. For all four cationic forms of the clay, the amount of initial water adsorption at 25°C and at low relative humidities was sensitive to the sample temperature during prior evacuation of water, less water being adsorbed by samples evacuated at 100°C compared with samples evacuated at 25°. For Ca- and Na-montmorillonite, these changes were reversible after several subsequent desorption/adsorption cycles, but recovery was not observed for the Li-SWy-1 clay, probably because of migration of Li<sup>+</sup> into the aluminosilicate structure.

**Key Words**—Adsorption, Enthalpy, Entropy, Montmorillonite, Relative humidity, Water.

### INTRODUCTION

During hydrocarbon exploration and production, serious problems are often encountered in smectite-rich mudrocks. These problems include borehole instability, commonly associated with the uptake of water by smectites from drilling fluids (Cheatham, 1984), and pore fluid pressures significantly greater than hydrostatic values. High pore-fluid pressures may be wholly or partly caused by water released during the diagenetic conversion of smectite to illite under deep burial conditions (Powers, 1967). Hydrated smectites may also strongly influence the stability of strike-slip faults in earthquake zones (Bird, 1984). A greater understanding of these and other natural phenomena requires a more detailed characterization of the state of hydration of smectites at elevated pressures and temperatures. Such a characterization should account quantitatively for the influence of stress, temperature, and pore fluid pressure and composition on the state of hydration.

An attempt to explore the PT phase diagram directly for the hydration of homoionic calcium montmorillonite by monitoring the fluid pressure change associated with the dehydration is reported elsewhere (Hall *et al.*, 1986). The method detected no change in the state of hydration at elevated pressures ( $\leq 20,000$  psi) to the maximum temperature investigated (185°C). These results are in accord with high-pressure XRD studies by Colten (1986), which showed no collapse of the basal spacing in a bilayer hydrate of sodium montmorillonite  $\leq 200^\circ\text{C}$  and pressures  $\leq 6700$  psi. Recent high-pressure differential thermal analysis data obtained by Koster van Groos and Guggenheim (1984,

1986, 1987) showed two dehydration reactions for natural (mixed ionic, Na-rich) and homoionic K-, Ca-, and Mg-montmorillonite. These reactions were separated typically by 60°–80°C in temperature, the higher temperature reaction usually giving rise to a shoulder on the more intense lower-temperature peak. At elevated pressures both peaks strongly shifted to higher temperatures, e.g., the lower temperature peak in Ca-montmorillonite increased from 177°C at 1 bar to 289°C at 21.8 bars, and  $\sim 400^\circ\text{C}$  at 100 bars. For each ionic form of the clay the enthalpy change associated with the second, higher temperature dehydration reaction was significantly larger than that associated with the lower temperature reaction. For example, for Ca-montmorillonite the values were about 12 and 23 kJ/mole for the first and second peaks, respectively.

The thermodynamic parameters (enthalpy and entropy of adsorption) that determine the range of stability of hydrated montmorillonites may also be obtained from water adsorption or desorption isotherms measured over a range of temperatures. Although extensive data already exist (e.g., Méring, 1946; Mooney *et al.*, 1952a, 1952b; Glaeser and Méring, 1954, 1968; Zettlemoyer *et al.*, 1955; Barshad, 1960; Fripiat *et al.*, 1965; Kijne, 1969; Keren and Shainberg, 1975, 1979; Ormerod and Newman, 1983), and some workers have evaluated the thermodynamic parameters, most of these studies were made using materials that are not now readily available. Moreover, the range of temperatures and/or vapor pressures covered by most of the available data is too limited to attempt a reliable extrapolation of the derived thermodynamic parameters up to the dehydration temperatures of the clay.

In this paper we report data obtained for the adsorption of water by homoionic preparations of montmorillonite SWy-1, from Crook County, Wyoming (van

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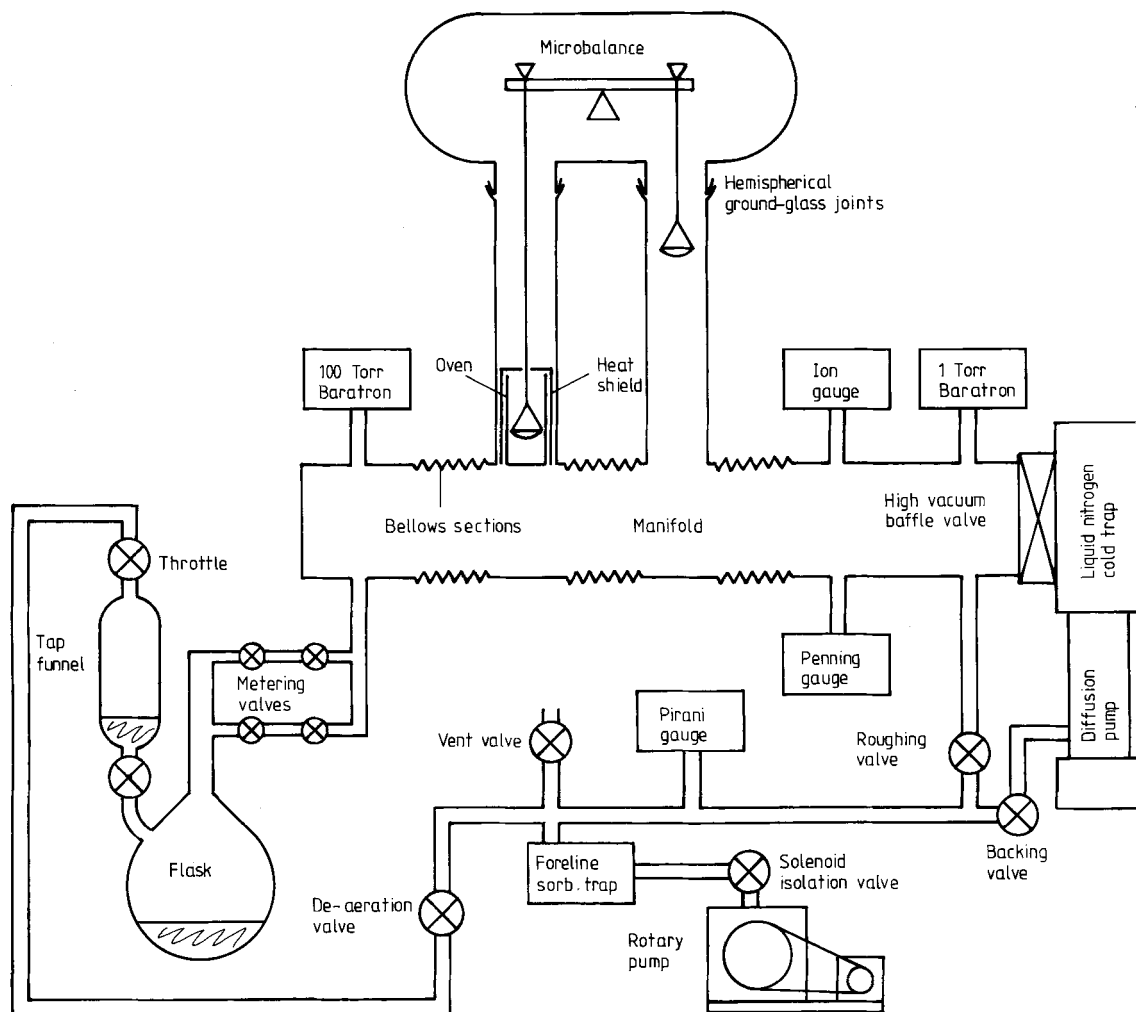


Figure 1. Schematic illustration of automated vacuum microbalance apparatus.

Olphen and Fripiat, 1979) at temperatures as high as 70°C. This clay was used in all of the high-pressure studies cited previously. From the adsorption isotherms, integral enthalpies and entropies of adsorption and estimated dehydration temperatures were calculated; these data are discussed in the context of the range of stability of hydrated smectites in sedimentary environments.

#### SAMPLES AND EXPERIMENTAL METHODS

The present studies were conducted using the automated vacuum microbalance system illustrated schematically in Figure 1. The microbalance, manufactured by C. I. Electronics Ltd., Salisbury, United Kingdom, has a total capacity of 1 g and a measuring range of 100 mg after electronic taring. It is connected by two wide-bore vertical glass tubes into a stainless steel vacuum manifold equipped with a conventional two-stage

(diffusion and rotary) pumping system having a liquid nitrogen cold trap. The vacuum system and manifold was constructed by CVT Ltd. Milton Keynes, United Kingdom. By pre-baking the metalwork, vacuums as low as  $10^{-7}$ – $10^{-8}$  mbar could be routinely achieved, typically in 2–3 days. One of the vertical glass tubes contained a small oven in which the sample was suspended. The oven was maintained at a constant temperature between ambient and  $150^{\circ}\text{C} \pm \sim 0.1^{\circ}\text{C}$  by a Eurotherm three-term temperature controller and two type-K thermocouples, one in physical contact with the oven and the other sensing temperatures in the vicinity of the sample pan.

After isolation of the evacuated system, a pre-selected vapor pressure was established via a flask containing de-aerated deionized water in communication with two pairs of miniature electro-pneumatic valves. The sequential operation of either pair of valves permitted the injection of a metered dose of water vapor into the vacuum manifold. The two dosing volumes

differed by a factor of 10, permitting coarse and fine pressure adjustment. The smaller dosing volume was about 5000 times smaller than the manifold volume. For an ambient temperature of 20°C, at which the saturated vapor pressure of water is about 18 Torr (24 mbar), this permits a minimum vapor pressure increment of 4  $\mu$ bar ( $3 \times 10^{-3}$  Torr). The vapor pressure in the manifold was sensed by two MKS Baratron absolute pressure transducers, covering low and high vapor-pressure ranges (as much as 1 and 100 Torr, respectively).

The vacuum manifold and dosing system were at ambient laboratory temperature, so that the maximum attainable water vapor pressure corresponded to the saturated vapor pressure of water at this temperature. This limitation implies that only partial isotherms (in terms of the range of relative vapor pressures) were measurable at elevated sample temperatures. Also, the automatic dosing system was only capable of measuring adsorption rather than desorption isotherms. One advantage of the system was that extremely small vapor pressures could be accurately measured and maintained, which helped in calculating thermodynamic parameters, such as enthalpies and entropies of adsorption, especially at lower water contents.

The apparatus was controlled by a Solartron Orion Delta data logger, which monitored the two thermocouples, an ambient temperature sensor, the two Baratrons, and the microbalance control unit, and delivered control signals to four metering valves. In practice, during the recording of an isotherm, after initial establishment of each chosen vapor pressure it was necessary to add make-up doses of water vapor regularly because adsorption reduced the pressure below its lower tolerance level. More details of the apparatus and methodology were reported by Astill *et al.* (1987).

The Crook County, Wyoming, montmorillonite (sample SWy-1, from the Source Clays Repository of The Clay Minerals Society) was described by van Olphen and Fripiat (1979). Samples of the "as received" clay were converted from the natural, mixed cationic form to homoionic Ca-, Li-, Na-, and K-exchanged forms in the following manner. The raw clay was suspended in deionized water and separated from coarser, silt-sized impurities of particle size  $\geq 2 \mu\text{m}$  e.s.d. by sedimentation or centrifugation. A chromatographic column having an internal volume of 300 ml was packed with 20–50-mesh beads coated with Biorad AG MP-50 macroporous cation-exchange resin. The resin was obtained as the hydrogen form and was converted to the required cationic form by passing a fourfold excess of a 1 M solution of the appropriate chloride through the column, followed by sufficient deionized water until a negative chloride test was obtained using acidified AgNO<sub>3</sub> solution. The total cation-exchange capacity of the packed column was  $\sim 500$  meq.

Four aliquots of 1% w/v aqueous suspensions were

prepared, each containing 5 g of  $\leq 2\text{-}\mu\text{m}$ -size clay on a dry-weight basis. Each was passed three times through a column saturated with a particular cation (Ca<sup>2+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, or K<sup>+</sup>). The cation-exchanged products were oven dried at 50°C and gently crushed with a pestle and mortar. The cationic contents of the clays were measured by means of a DIONEX ion chromatograph system using the ammonium displacement method. The initial  $\leq 2\text{-}\mu\text{m}$ -size SWy-1 clay was found to have a total CEC of 81 meq/100 g, comprising 48 meq of Na<sup>+</sup>, 1.2 meq of K<sup>+</sup>, 20 meq of Ca<sup>2+</sup>, and 11 meq of Mg<sup>2+</sup>. Data tabulated by van Olphen and Fripiat (1979) indicate a mean CEC of  $\sim 76$  meq/100 g for the untreated specimen (i.e., including silt-sized impurities). Analyses of the four cation-exchanged samples showed that the Ca<sup>2+</sup> form contained more than 98% calcium and only a small amount of magnesium, but that the monovalent clays were less completely (85–90%) exchanged.

Isotherms were recorded starting typically with  $\sim 70$  mg dry clay. For the Ca-, Li-, and Na-montmorillonites, isotherms were measured at four temperatures ranging from 25° to 70°C. For K-montmorillonite, isotherms were measured at 25° and 40°C only, due to the limited extent of adsorption at elevated temperatures. For each of the four exchange forms the isotherms at 25°C were recorded on samples maintained at both 25° and 100°C during evacuation-baking of the manifold, in the second case after waiting for the necessary cooling to take place prior to measurement of the water uptake. The initial water uptake after baking the sample at 100°C was found to be substantially lower (see Results and General Discussion section).

#### CALCULATION OF THERMODYNAMIC PARAMETERS

Adsorption isotherm measurements at different temperatures permit the changes in the thermodynamic properties of the system due to the adsorption process to be evaluated. In the conventional approach, a one-component (adsorbate) system is assumed, the substrate being assumed to be inert, so that derived enthalpies and entropies of adsorption formally represent the changes in the properties of water between the bulk liquid and the adsorbed state (Hill, 1949, 1950; Hill *et al.*, 1951). As pointed out by a number of previous workers (e.g., van Olphen, 1965; Keren and Shainberg, 1980; Sposito and Prost, 1982), however, for smectites the "inert substrate" assumption is certainly not valid. This implies that the values of any thermodynamic parameter computed from isotherms or calorimetric data must represent the overall effect of water sorption, parting of the unit layers, and changes in relative position between the layers and the exchange ions.

From adsorption isotherms recorded at different temperatures, either differential or integral enthalpies and entropies of adsorption may be obtained. All four may ultimately be obtained from the Clausius-Clapeyron

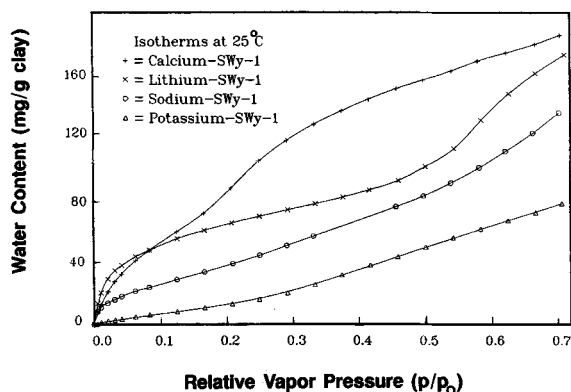


Figure 2. Adsorption isotherms for water on Ca-, Li, Na, and K-SWy-1 montmorillonite at 25°C.

equation by evaluating terms of the type  $\theta \ln p / \partial(1/T)$ , where  $p$  is the equilibrium vapor pressure and  $T$  the absolute temperature. Hill (1949, 1950) pointed out that for an inert substrate the true integral equilibrium enthalpy and entropy changes, here denoted  $\Delta H$  and  $\Delta S$  respectively, are those that are computed at constant spreading pressure, rather than the differential or isosteric quantities (which are evaluated at constant gravimetric water content). See also van Olphen (1965) for a discussion of the relationship between these quantities.

The spreading pressure,  $\phi$ , is defined by the equation

$$\phi = RT/MA \int_0^p \theta d \ln p, \quad (1)$$

where  $R$  is the gas constant,  $M$  is the molecular weight of the adsorbate,  $A$  is the specific surface area of the substrate, and  $\delta$  is the gravimetric water content (g H<sub>2</sub>O/g dry clay) (Keren and Shainberg, 1980). Physically,  $\phi$  represents the difference in the surface tension between dry and wet systems. For the SWy-1 clay, van Olphen and Fripat's (1979) specific surface area of 663 m<sup>2</sup>/g was used in the calculations. Although the thermodynamic parameters are evaluated at constant values of  $\phi$ , they are independent of the absolute values of  $\phi$ . Thus, any variation of  $A$  with cation type will have no effect on the calculated thermodynamic quantities, since for each cation-exchange form any error in  $A$  will change  $\phi$  at each temperature by the same factor.

The isotherm at each temperature gives  $\theta$  as a function of  $p$ , from which  $\phi$  may be computed as a function of  $p$  using Eq. (1). By determining the vapor pressure ratios  $x_1$  and  $x_2$  corresponding to constant values of  $\phi$  for isotherms at absolute temperatures  $T_1$  and  $T_2$ , the required thermodynamic functions were given by (Hill, 1949, 1950; Hill *et al.*, 1951):

$$\Delta H = \left[ \frac{T_1 T_2}{T_2 - T_1} R \ln \left( \frac{x_1}{x_2} \right) \right]_{\phi}, \quad (2)$$

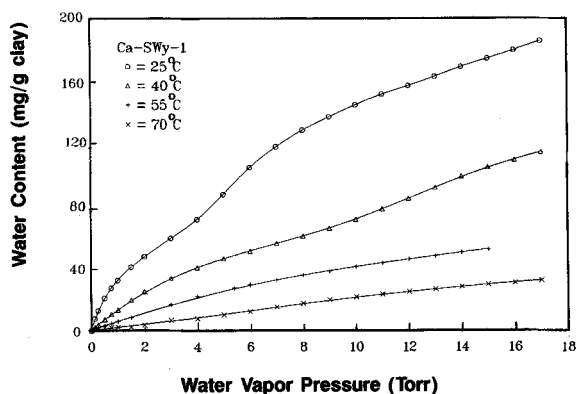


Figure 3. Adsorption isotherms for water on Ca-SWy-1 montmorillonite at 25°, 40°, 55°, and 70°C.

and

$$\Delta S = \frac{R}{2} \left[ \frac{T_1 + T_2}{T_2 - T_1} \ln \left( \frac{x_1}{x_2} \right) - \ln(x_1 x_2) \right]_{\phi}, \quad (3)$$

In the present study, the values of  $\phi$  were calculated by performing the integral in Eq. (1) numerically, the accuracy of the calculation being enhanced by making a linear extrapolation of the  $(\theta, p)$  data to very small values of  $p$ .

For a liquid/vapor phase change involving one mole of any substance the vapor pressure  $p$  and temperature  $T$  are related by the equation

$$\frac{d \ln p}{d(1/T)} = -\frac{\Delta H}{R}, \quad (4)$$

where  $\Delta H$  is the change in enthalpy per mole of material changing phase (Moore, 1972). A plot of  $\ln p$  vs.  $1/T$  should therefore be linear and of gradient  $-\Delta H/R$ . For the liquid/vapor phase change of bulk water,  $\Delta H$  represents the enthalpy of vaporization or condensation. For the adsorption of water vapor by a solid substrate,  $\Delta H$  represents the net enthalpy change in going from bulk vapor to adsorbed liquid. This may be considered as two stages: (1) vapor to bulk liquid, and (2) bulk liquid to adsorbed liquid, so that  $\Delta H$  now represents the sum of the enthalpy of condensation and the enthalpy of adsorption. This means that a plot of  $\ln p$  vs.  $1/T$  from adsorption isotherm data recorded at different temperatures will have a different slope from the plot for bulk water. The temperature at which the two plots intersect is that above which the hydrated phase of the solid will not occur, even in the presence of a saturated vapor, i.e., the thermodynamic equilibrium dehydration temperature of the hydrated substance.

## RESULTS AND GENERAL DISCUSSION

Adsorption isotherms for the four homoionic exchange forms of the SWy-1 montmorillonite are illus-

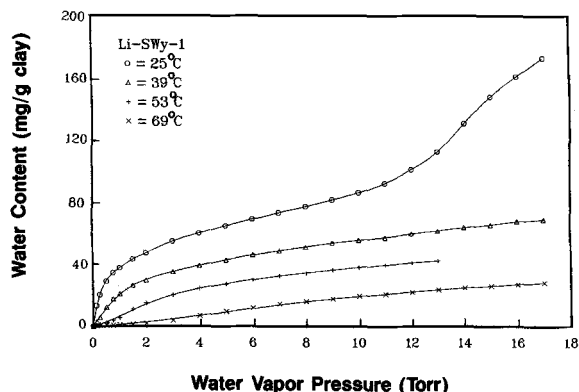


Figure 4. Adsorption isotherms for water on Li-SWy-1 montmorillonite at 25°, 39°, 53°, and 69°C.

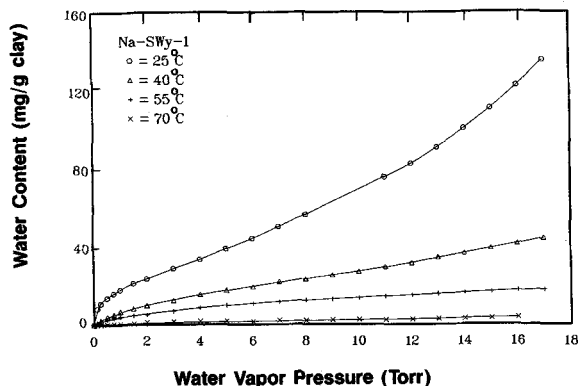


Figure 5. Adsorption isotherms for water on Na-SWy-1 montmorillonite at 25°, 40°, 55°, and 70°C.

trated in Figure 2. Monovalent cation-exchange forms show increasing water adsorption in the order  $K < Na < Li$ , i.e., in the order of increasing ionic polarizability or charge: size ratio. These data graphically illustrate the influence of the process of cation hydration on the degree of water uptake by montmorillonite.

At a relative vapor pressure  $p/p_0 \leq 0.7$ , the Ca-exchanged clay has a larger water content for a given  $p/p_0$  than any of the monovalent exchange forms. Isotherms for both the Ca- and Li-exchanged forms show inflections at values of  $p/p_0$  of  $\sim 0.2$  and  $\sim 0.5$ , respectively, in line with previous data (Mooney *et al.*, 1952b). The variation of water adsorption with temperature between 25° and 70°C is illustrated for the Ca-, Li-, and Na-exchanged forms in Figures 3, 4, and 5 respectively. Figure 6 illustrates the adsorption isotherms for K-montmorillonite at 25° and 39°C, the only two temperatures for which data were obtained. Table 1 lists values for the saturated vapor pressure of water at 25°, 40°, 55°, and 70°C, to enable the data to be interpreted in terms of relative vapor pressures  $p/p_0$ .

Figures 7 and 8 show the dependence of the integral enthalpy and entropy of adsorption on gravimetric water content for the Na-, Li-, and Ca-SWy-1-montmorillonite, compared with the data of Keren and Shainberg (1980) for the Ca- and Na-exchanged forms of the API No. 25 Wyoming bentonite. All sets of values of the enthalpy change  $\Delta H$  are negative, corresponding to exothermic hydration reactions, and also decrease in magnitude with increasing water content. Our values

for Na-montmorillonite at lower water contents are somewhat more negative (i.e., larger absolute values) than those derived by Keren and Shainberg, the two sets of data becoming closer at slightly higher water contents. Conversely our values for the Ca-SWy-1 clay are less negative than Keren and Shainberg's values; however, in both sets of data  $\Delta H$  decreases more sharply with increasing water content for Na-montmorillonite than for Ca-montmorillonite.

At low water contents, the enthalpy change for Li-montmorillonite is comparable to that for Na-montmorillonite, whereas at somewhat higher water contents (30–65 mg water/g clay) the enthalpy change for the Li clay is substantially higher. This may be interpreted in the following manner. Below a relative vapor pressure  $p/p_0 \sim 0.1$ , both Na- and Li-montmorillonites are fully collapsed (MacEwan and Wilson, 1980), so that the initial adsorption of water occurs at external siloxane surfaces, which are similar for both samples. At higher water contents, at which the effects of cation hydration come into play, the enthalpies of adsorption are greater for Li than for Na, consistent with the stronger polarizability of the smaller Li cations (ionic radii: Li = 0.60 Å; Na = 0.95 Å).

Table 1. Values of the saturated vapor pressure of water at the temperatures of the isotherm measurements.<sup>1</sup>

Temperature (°C)	Saturated vapor pressure (Torr)
25	23.75
40	69.30
55	118.04
70	233.70

<sup>1</sup> 1 Torr = 1 mm of mercury = 0.1334 kN/m<sup>2</sup>.

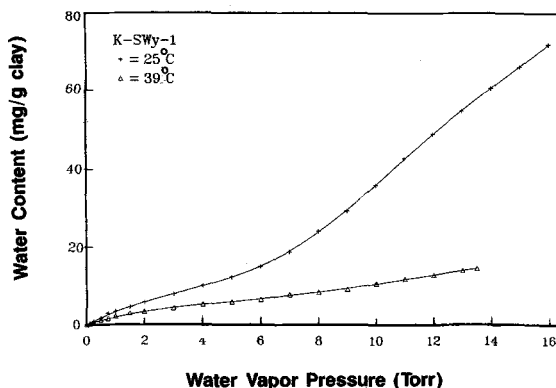


Figure 6. Adsorption isotherms for water on K-SWy-1 montmorillonite at 25° and 39°C.



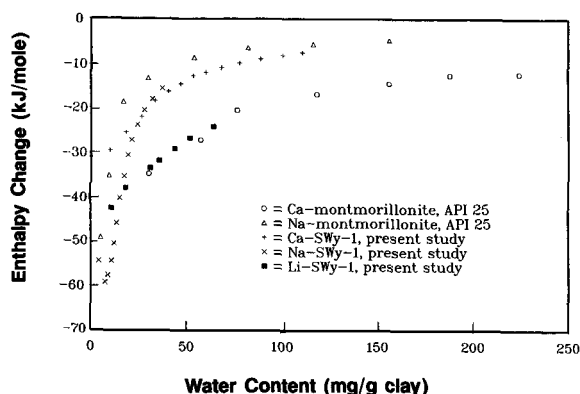


Figure 7. Change of integral enthalpy for water adsorption by Ca-, Li-, and Na-Swy-1 montmorillonite as a function of gravimetric water content, compared with the data of Keren and Shainberg (1980) for Ca- and Na-exchange forms of Wyoming (API 25) montmorillonite.

From the known cation-exchange capacity of 81 meq/100 g and the gravimetric water content the numbers of adsorbed water molecules per exchange ion may readily be calculated. For the Ca-SWy-1 clay our data gave values of  $\Delta H$  of the order of 25, 15, and 12 kJ/mole at water contents of 3, 6, and 9 molecules per exchange cation, respectively. These values may be compared with Koster van Groos and Guggenheim's (1987) values of  $\sim 12$  and 23 kJ/mole for the first and second dehydration reactions, respectively, from their high-pressure differential thermal analysis data. At a water content corresponding to 3 molecules per monovalent exchange ion, values of  $\Delta H$  of  $\sim 15$  and 30 kJ/mole for Na-SWy-1 and Li-SWy-1 were obtained, respectively. The former is between the values of  $\Delta H$  for the first and second dehydration reactions of Na-rich SWy-1 montmorillonite (Koster van Groos and Guggenheim, 1986).

All integral entropy changes  $\Delta S$  were also found to be negative consistent with an increase in the degree of ordering of the system due to the adsorption process, as concluded by Keren and Shainberg (1980) and other workers. The trends are qualitatively very similar to the enthalpy data. The reasons for the differences between the thermodynamic parameters for the Ca-exchanged forms of the API No. 25 and SWy-1 montmorillonites is not clear. Apart from the fact that the API No. 25 clay has a cation-exchange capacity ( $\sim 90$  meq/100 g) slightly greater than that of the SWy01 montmorillonite, they are otherwise similar.

The influence of pre-drying temperature on the 25°C adsorption isotherm of the Ca-, Na-, and K-clays is illustrated in Figure 9. For each exchange form, at lower relative humidities less water is adsorbed at a given relative humidity on the clay previously dried at 100°C at high vacuum. At higher relative humidities each pair of isotherms tend to converge. These results are prob-

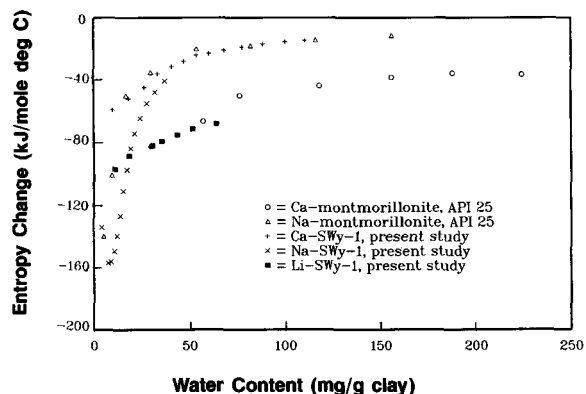


Figure 8. Change of integral entropy for water adsorption by Ca-, Li-, and Na-SWy-1 montmorillonite as a function of gravimetric water content, compared with the data of Keren and Shainberg (1980) for Ca- and Na-exchange forms of Wyoming (API 25) montmorillonite.

ably due to a temporary loss of some of the more energetic adsorption sites, probably associated with the removal of the last traces of water and the embedment of cations into the ditrigonal cavities of the siloxane surface. At greater  $p/p_0$  values, corresponding to more extensive cation hydration, the adsorption capacity apparently never recovered. For the Ca-clay the recovery of adsorption capacity was only obtained after a number of additional desorption/adsorption cycles at 25°C (see Figure 10). An initial 25°C isotherm was recorded after vacuum drying at 100°C. The sample was re-evacuated at 25°C, after which a second 25°C isotherm was recorded. The original isotherm was not followed, and several more cycles of wetting and re-drying under vacuum at 25°C were necessary before the adsorption isotherm was reproduced exactly and coincided with the isotherm of the unbaked clay. A similar cyclic recovery of adsorption capacity was observed also for the Na-exchanged clay.

The reasons for the loss and subsequent recovery of adsorption capacity are not entirely clear, but may be associated with slow rehydration of cations strongly bonded directly to oxygen atoms of the siloxane surfaces. Our data support a hysteresis in the heats of wetting of montmorillonite at low  $p/p_0$ , as observed by Zettlemoyer *et al.* (1955). Qualitatively similar results were also obtained by van Olphen (1969) in studies on the dependence of baking temperature on water adsorption by Mg-vermiculite.

In the present study, for Li-montmorillonite a large difference in water uptake between samples pre-baked at 25° and 100°C was observed, which appeared to be largely irreversible (see Figure 11), at least over one subsequent cycle of desorption and adsorption. The irreversibility was probably due to thermally activated migration of the smaller  $\text{Li}^+$  cations from the interlamellar space into vacant Al octahedral sites (Hoffmann

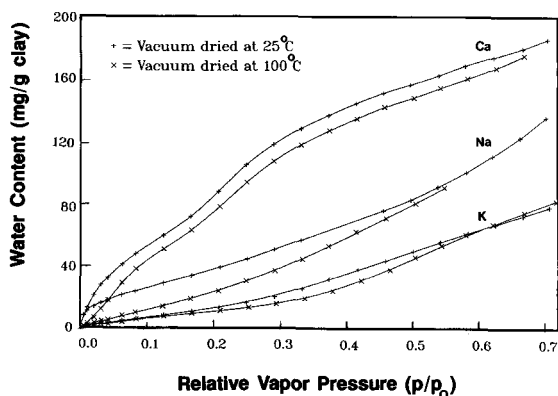


Figure 9. Influence of evacuation temperature on the 25°C adsorption isotherms for Ca-, Na-, and K-SWy-1 montmorillonite.

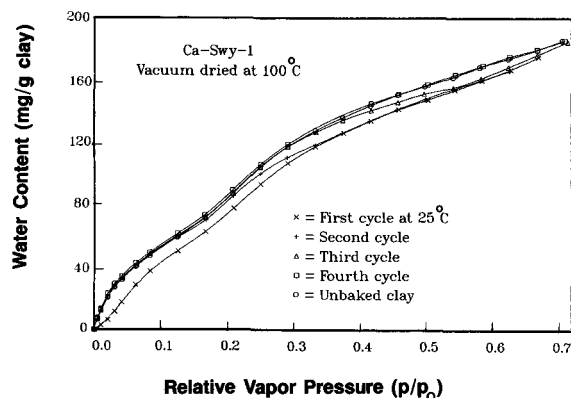


Figure 10. Recovery of water adsorption capacity by Ca-SWy-1 montmorillonite at 25°C after initial evacuation at 100°C.

and Klemen, 1950). Whether or not such phenomena were reversible, they clearly exerted a marked effect on the shape of the water adsorption isotherm. Variability of thermal treatment of the sample should therefore be avoided.

The predicted dehydration temperatures for the Ca-, Li-, Na-, and K-exchanged SWy-1 montmorillonite in the presence of deionized water were estimated from van't Hoff plots, described by Eq. (4) above. The clay-water data were obtained for an arbitrary small water content of 20 mg/g of dry clay. Values for the saturated vapor pressure of bulk water as a function of temperature were taken from Kaye and Laby (1973). The predicted dehydration temperatures are all in the range 170°–265°C and decrease in the order Ca > Li > Na > K. These values agree reasonably well with dehydration temperatures from ambient pressure differential thermal analysis data (van Olphen and Fripiat, 1979; Koster van Groos and Guggenheim, 1987).

The results, together with the high-pressure X-ray powder diffraction studies of Colten (1986) and the high-pressure differential thermal analysis work of Koster van Groos and Guggenheim (1984, 1986, 1987) suggest that the thermal stability of the last two interlamellar water bilayers in montmorillonite is greater than the typical temperatures at which smectite disappears and diagenetic illite forms. Thus, as discussed by Hall *et al.* (1986), in most sedimentary rocks the loss of the last two interlamellar water layers from smectites is most probably normally associated with the process of illitization, usually at a temperature substantially below the thermodynamic dehydration temperature of smectite. The thermodynamic considerations provide an upper stability limit for hydrated montmorillonite, which might conceivably be approached in hot but relatively young sediments, e.g., in hydrothermal environments, in which there has been insufficient time for illitization to have occurred, or

where the illitization has been kinetically hindered, as, e.g., in K-poor environments.

Care should, however, be exercised in extrapolating these results to real subsurface geological environments for a number of reasons. Either pore fluid pressures significantly lower than lithostatic pressures or high pore fluid salinities significantly reduce the Gibbs free energy of pore water relative to the interlayer water of the smectite, and, hence, lower the equilibrium temperature for dehydration. Nevertheless, it may be tentatively concluded that, in K-poor sedimentary environments, hydrated montmorillonite is likely to be stable over most of the ranges of stresses and temperatures normally encountered.

## SUMMARY

Adsorption isotherms for water on Ca-, Li-, Na-, and K-exchanged forms of SWy-1 Wyoming montmorillonite recorded at temperatures up to 70°C dif-

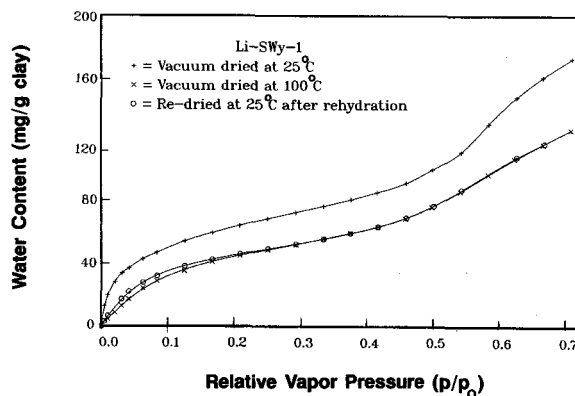


Figure 11. Irreversible loss of adsorption capacity by Li-SWy-1 montmorillonite at 25°C. + = Initial isotherm after evacuation at 25°C; X = isotherm after evacuation at 100°C; O = repeated isotherm after re-evacuation at 25°C.

ferred markedly with cation type. Isotherms recorded at 25°C were influenced by the temperature of the sample during initial vacuum desiccation. For the Ca- and Na-exchanged forms, these changes were found to be reversible after several further desorption/adsorption cycles, but reversibility was not achieved for Li-montmorillonite, probably due to migration of the Li<sup>+</sup> ions into vacant octahedral sites.

For the Ca-, Li-, and Na-clays the integral entropies and enthalpies of adsorption were negative, but decreased in magnitude with increasing gravimetric water content, in qualitative agreement with earlier data (e.g., Keren and Shainberg, 1980). Calculated thermodynamic dehydration temperatures were in the range 170–265°C, well above the usual temperature range of the smectite-to-illite transformation, suggesting that the latter process probably controls the loss of the interlayer water from smectites under deep-burial conditions.

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#### REFERENCES

- Astill, D. M., Hall, P. L., and McConnell, J. D. C. (1987) An automated vacuum microbalance for measurement of adsorption isotherms: *J. Phys. E: Sci. Instrum.* **20**, 19–21.
- Barshad, I. (1960) Thermodynamics of water adsorption and desorption on montmorillonite: in *Clays and Clay Minerals, Proc. 8th Natl. Conf., Norman, Oklahoma, 1959*, Ada Swineford, ed., Pergamon Press, New York, 84–101.
- Bird, P. (1984) Hydration phase diagrams and friction of montmorillonite under laboratory and geologic conditions, with implications for shale compaction, slope stability, and strength of fault gouge: *Tectonophysics* **107**, 235–260.
- Cheatham, J. B. (1984) Wellbore stability: *J. Petrol. Tech.*, 889–896.
- Colten, V. A. (1986) Hydration states of smectites in NaCl brines at elevated pressures and temperatures: *Clays & Clay Minerals* **34**, 385–389.
- Fripiat, J. J., Jelli, A., Poncelet, G., and André, J. (1965) Thermodynamic properties of adsorbed water molecules and electrical conduction in montmorillonite and silicates: *J. Phys. Chem.* **69**, 2185–2197.
- Glaeser, R. and Méring, J. (1954) Hydration isotherms of bi-ionic montmorillonites (Na, Ca): *Clay Miner. Bull.* **2**, 188–193.
- Glaeser, R. and Méring, J. (1968) Homogeneous hydration domains of the smectites: *Compt. Rend. Acad. Sci. Paris* **267**, 436–466.
- Hall, P. L., Astill, D. M., and McConnell, J. D. C. (1986) Thermodynamic and structural aspects of the dehydration of smectites in sedimentary rocks: *Clay Miner.* **21**, 633–648.
- Hill, T. L. (1949) Statistical mechanics of adsorption V. Thermodynamics and heat of adsorption: *J. Chem. Phys.* **17**, 520–535.
- Hill, T. L. (1950) Statistical mechanics of adsorption. IX. Adsorption thermodynamics and solution thermodynamics: *J. Chem. Phys.* **18**, 246–256.
- Hill, T. L., Emmett, P. M., and Joyner, L. E. (1951) Calculations of thermodynamic functions of adsorbed molecules from adsorption isotherm measurements. Nitrogen on graphon: *J. Amer. Chem. Soc.* **73**, 5102–5107.
- Hoffmann, U. and Klemen, R. (1950) Effect of heating on Li-bentonite: *Z. Anorg. Chem.* **262**, 95–99.
- Kaye, G. W. C. and Laby, T. H. (1973) *Tables of Physical and Chemical Constants*, 14th ed., Longman, London, p. 173.
- Keren, R. and Shainberg, I. (1975) Water vapor isotherms and heat of immersion of Na/Ca-montmorillonite systems—I: Homoionic clay: *Clays & Clay Minerals* **23**, 193–200.
- Keren, R. and Shainberg, I. (1979) Water vapor isotherms and heat of immersion of Na/Ca-montmorillonite systems—II: Mixed systems: *Clays & Clay Minerals* **27**, 145–151.
- Keren, R. and Shainberg, I. (1980) Water vapor isotherms and heat of immersion of Na- and Ca-montmorillonite systems. III. Thermodynamics: *Clays & Clay Minerals* **28**, 204–210.
- Kijne, J. (1969) On the interaction of water molecules and montmorillonite surfaces: *Soil Sci. Soc. Amer. Proc.* **33**, 539–543.
- Koster van Groos, A. F. and Guggenheim, S. (1984) The effect of pressure on the dehydration reaction of interlayer water in Na montmorillonite (SWy-1): *Amer. Mineral.* **69**, 872–879.
- Koster van Groos, A. F. and Guggenheim, S. (1986) Dehydration of K-exchanged montmorillonite at elevated temperatures and pressures: *Clays & Clay Minerals* **34**, 281–286.
- Koster van Groos, A. F. and Guggenheim, S. (1987) Dehydration of a Ca- and a Mg-exchanged montmorillonite (SWy-1) at elevated pressures: *Amer. Mineral.* **72**, 292–298.
- MacEwan, D. M. C. and Wilson, M. J. (1980). Interlayer and intercalation complexes of clay minerals: in *Crystal Structures of Clay Minerals and their X-ray Identification*, G. W. Brindley and G. Brown, eds., Mineralogical Society, London, 197–248.
- Méring, J. (1946) On the hydration of montmorillonite: *Trans. Faraday Soc.* **42B**, 205–219.
- Mooney, R. W., Keenan, A. G., and Wood, L. A. (1952a) Adsorption of water by montmorillonite. I. Heat of desorption and application of BET theory: *J. Amer. Chem. Soc.* **74**, 1367–1371.
- Mooney, R. W., Keenan, A. G., and Wood, L. A. (1952b) Adsorption of water by montmorillonite. II. Effect of exchangeable ions and lattice swelling as measured by X-ray diffraction: *J. Amer. Chem. Soc.* **74**, 1372–1374.
- Moore, W. J. (1972) *Physical Chemistry*, 5th ed., Longman, London, p. 212.
- Ormerod, E. C. and Newman, A. C. D. (1983) Water sorption on Ca-saturated clays. II. Internal and external surfaces of montmorillonite: *Clay Miner.* **18**, 289–299.
- Powers, M. C. (1967) Fluid release mechanisms in compacting marine mudrocks and their importance in oil exploration: *Amer. Assoc. Petrol. Geol. Bull.* **51**, 1240–1254.
- Sposito, G. and Prost, R. (1982) Structure of water adsorbed on smectites: *Chemical Reviews* **82**, 553–573.
- van Olphen, H. (1965) Thermodynamics of interlayer adsorption of water in clays. I. Sodium vermiculite: *J. Colloid Sci.* **20**, 822–837.



- van Olphen, H. (1969) Thermodynamics of interlayer adsorption of water in clays. II. Magnesium vermiculite: in *Proc. 3rd Int. Clay Conference, Tokyo, 1969, Vol. I*, L. Heller, ed., Israel Prog. Sci. Transl., Jerusalem, 649–657.
- van Olphen, H. and Fripiat, J. J. (1979) *Data Handbook for Clay Minerals and other Non-metallic Minerals*: Pergamon Press, Oxford, 346 pp.
- Zetlemoyer, A. C., Young, E. J., and Chessick, J. (1955) Studies of the surface chemistry of silicate minerals. III. Heat of immersion of bentonite in water: *J. Phys. Chem.* **59**, 962–966.

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