

## PROPERTIES OF WATER IN CALCIUM- AND HEXADECYLTRIMETHYLAMMONIUM-EXCHANGED BENTONITE

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**Abstract**—Dynamical and thermodynamic properties of water at room temperature in Ca- and hexadecyltrimethylammonium- (HDTMA) exchanged bentonite were determined for 4 different water contents (~0.03–0.55 g water g<sup>-1</sup> clay). Incoherent quasi-elastic neutron scattering (QENS) was used to measure the translational and rotational mobility of water in the clays, while chilled mirror dewpoint psychrometry measured water activity of the samples, differential scanning calorimetry (DSC) provided information about the temperature of dehydration and X-ray diffraction (XRD) quantified layer spacings for the clays. The neutron scattering data were fit to a jump diffusion model that yielded mean jump lengths, jump diffusion residence times and rotational relaxation times for water in the clays. Mean jump lengths were quite similar for the 2 different cation saturations at equivalent water contents, and decreased with increasing water content. The fitted jump lengths ranged from 0.27–0.5 nm and were 2–4 times larger than that found for bulk water (0.13 nm). Jump diffusion residence times were 3–30 times longer than that for bulk water (1.2 ps) and also decreased with increasing water content. The residence times were somewhat shorter for HDTMA-clay as compared with Ca-clay at equivalent water contents. Rotational motion was less strongly influenced than translational motion by the presence of the clay surface. The energy state of water in the 2 cation saturations were quite different; dehydration temperatures for the HDTMA-clay were approximately 30 °C lower than the Ca-clay at equal water contents, while water activities, as  $P/P^0$ , were up to 0.6 units higher. A linear relationship was found between water activity and the translational diffusion coefficient, although at the highest water content, the diffusion coefficient of water for the HDTMA-clay was approximately 30% higher than that measured for bulk water.

**Key Words**—Bentonite, Diffusion, HDTMA, Neutron Scattering, Water.

### INTRODUCTION

Smectitic clays play important roles in many natural and engineered systems. Smectites are notable for their high cation exchange capacities, large surface areas, and expansibility upon hydration. Their presence in relatively modest quantities in soils imparts important hydraulic and chemical properties that ultimately influence a range of processes, including water infiltration, runoff, and retention and transport of contaminants in soils.

Smectite clays also have important roles in a variety of waste management and treatment strategies. Smectites are often compacted and used as liners in landfills, in bentonite slurry walls and in other waste containment systems due to their low hydraulic conductivities. Clays have also been modified to enhance their reactivity towards particular contaminants. For example, the surfaces of clays have been modified by addition of alkyl cations to change the polarity of the surfaces and thereby enhance retention of organic pollutants (Mortland et al. 1986; Srinivasah and Fogler 1990).

It is well established that the properties of water at the mineral-water and air-water interfaces deviate substantially from that of the bulk. In classic studies by Low and others, it has been shown that water absorbed to minerals bears a higher viscosity (Low 1976), heat capacity (Oster and Low 1964) and lower density (An-

derson and Low 1958) than that of bulk water. Spectroscopic studies also demonstrate significant surface effects on adsorbed water. NMR relaxation measurements indicate a greatly reduced mobility of surface water molecules (Resing 1976; Cruz et al. 1978; Wong and Ang 1985). These observations are supported by dielectric relaxation measurements, where relaxation times for adsorbed water (for example, on hematite) range from about 1 to 10<sup>-4</sup> s, values substantially higher than that for bulk liquid water (10<sup>-10</sup> s) (McCafferty and Zettlemoyer 1971). Results from other iron oxyhydroxides, kaolinite and zeolites further support the notion of a reduced mobility, ice-like structure of water with dielectric constants substantially different than bulk water (surface values of 2–15 vs. 80 for bulk) (Kaneko et al. 1975; Foster and Resing 1976; Hall and Rose 1978). Furthermore, the acidity of water at the mineral-water interface can be quite different than that of the bulk, wherein degree of dissociation of adsorbed water is about 2 orders of magnitude larger than in bulk liquid water (Sposito 1984). These properties, in turn, affect the nature, rate and extent of interfacial reactions with solutes, including development of the electrical double layer (Sposito 1984), the pK of weak organic acids and bases (Bhattacharyya et al. 1987; Zhao et al. 1990) and the accumulation and orientation of organic solutes at interfaces (Bell et al. 1992).

While properties of water at the mineral-water interface have been studied, the properties of water near

a surface exchanged with alkyl cations have not been evaluated. The objectives of this study, then, were to quantify the dynamical and thermodynamic properties of water in a Ca- and HDTMA-exchanged bentonite.

### EXPERIMENTAL APPROACH

The properties of water at varying gravimetric water contents in Ca- and HDTMA-exchanged bentonite were quantified using incoherent QENS, DSC and chilled mirror dewpoint psychrometry.

All experiments were conducted using reference Belle Fourche, SD bentonite. Approximately 50 g of bentonite were wetted with ethanol and ground to <2  $\mu\text{m}$  using an agate mortar and pestle. Samples were initially exchange-phase saturated with Ca by multiple equilibrations with 1 M  $\text{CaCl}_2$  solutions. Excess  $\text{CaCl}_2$  was removed by resuspension in deionized water followed by centrifugation and disposal of the supernatant; this was repeated for a total of 4 times. The cation exchange capacity (CEC) of the clay was determined by triplicate extraction of subsamples with 1 M  $\text{NH}_4\text{Cl}$  followed by centrifugation and compositing of the supernatants, and extractant analysis for Ca by atomic absorption spectrophotometry. The CEC for the clay, after correction for entrained solution in the initial sample, was determined to be 102 cmol (+)  $\text{kg}^{-1}$ , in good agreement with other reported values for the Belle Fourche clays of 100–120 cmol (+)  $\text{kg}^{-1}$  (Grim and Guven 1978). Subsamples were then equilibrated with HDTMA following Boyd et al. (1988) to yield about 100% exchange phase saturation. Following exchange, clays were resuspended in deionized water followed by centrifugation to remove excess salts and dried at 60  $^\circ\text{C}$ . The clays were gently disaggregated during drying using mortar and pestle. Calcium and HDTMA-exchanged clays were then brought to gravimetric water contents of  $\sim 0.03$ , 0.1, 0.3 and 0.55 g  $\text{H}_2\text{O g}^{-1}$  dry weight clay. Vapor equilibrations with salt solutions aided in the preparation of the lowest water content samples, while direct addition of water with a microsyringe was used for the higher water contents. Final water contents were determined on subsamples heated overnight at 110  $^\circ\text{C}$ .

Quasi-elastic neutron scattering experiments were conducted to quantify the mobility of water in the Ca- and HDTMA-saturated clays as a function of water content. QENS is ideally suited for studies of the mobility of water in clays because of the weak scattering of neutrons by atoms (that is, useful for bulk measurements) and because of the relatively large scattering cross section of H relative to other atoms in the sample. A scattering proton that is undergoing diffusive motion yields a scattered neutron with, effectively, a small Doppler shift. Analysis of the (quasi-elastic) scattering provides information about both the time-scale and the geometry of the motion (Cebula et al. 1981; Teixeira et al. 1985; Cavatorta et al. 1994).

The QENS experiments were conducted at the Intense Pulsed Neutron Source (IPNS) at the Department of Energy's Argonne National Laboratory using an inverted geometry time-of-flight spectrometer (Newsam et al. 1990). All samples were analyzed at room temperature (22–24  $^\circ\text{C}$ ). QENS spectra were collected at 9 scattering angles (25–145  $^\circ 2\theta$ ), corresponding to a momentum transfer range of 5–23.5  $\text{nm}^{-1}$ . The intensity of scattered neutrons were measured at energy transfers of  $-1.5$  to 5 meV, at an energy resolution for the spectrometer of 70  $\mu\text{eV}$ , and referenced against energy resolution functions determined for the Ca- and HDTMA-clays at 15 K. The QENS spectra were then fit to the jump-diffusion model of Teixeira et al. (1985), which relates the incoherent scattering intensity  $S_{\text{inc}}$ , which is a function of momentum transfer,  $Q$ , and energy transfer,  $\omega$ , to the vibrational, rotational and translational motion of the proton:

$$S_{\text{inc}}(Q, \omega) = \exp(-Q^2 \langle u^2 \rangle) S_{\text{trans}}(Q, \omega) \otimes S_{\text{rot}}(Q, \omega) \quad [1]$$

where  $\langle u^2 \rangle$  is the mean square vibrational displacement of the proton about an equilibrium position, and  $S_{\text{trans}}(Q, \omega)$  and  $S_{\text{rot}}(Q, \omega)$  are the scattering due translational and rotational motions, respectively. The scattering due to translation can be expanded to:

$$S_{\text{trans}}(Q, \omega) = \frac{1}{\pi} \frac{\Gamma_t(Q)}{\omega^2 + \Gamma_t^2(Q)} \quad [2]$$

with

$$\Gamma_t(Q) = \frac{D_t Q^2}{1 + D_t Q^2 \tau_0} \quad [3]$$

where  $D_t$  and  $\tau_0$  are the translational diffusion coefficient and the residence time between jumps, respectively. Scattering due to rotational motion can be written as:

$$S_{\text{rot}}(Q, \omega) = \sum_{\ell} (2\ell + 1) j_{\ell}^2(Qa) \frac{\ell(\ell + 1)\Gamma_r}{\omega^2 + (\ell(\ell + 1)\Gamma_r)^2} \quad [4]$$

where  $j_{\ell}(Qa)$  are spherical Bessel functions and  $a$  is the radius of rotation (Teixeira et al. 1985; Cavatorta et al. 1994). Equations [1–4] were then fitted to measured  $S(Q, \omega)$  to yield jump diffusion lengths and translational and rotational relaxation rates for water at varying water contents in the samples.

The clay samples were further characterized using XRD techniques using a Siemens Model D-500 X-ray diffractometer. The diffractometer was scanned from 2–32  $^\circ 2\theta$  at a step speed of 0.02  $^\circ 2\theta \text{ s}^{-1}$  using a  $\text{CuK}\alpha$  source ( $\lambda = 0.1542 \text{ nm}$ ). The activity of water in the samples were measured using a Decagon Water Activity meter which uses the chilled mirror dewpoint technique to quantify the vapor pressure of water in equilibrium with the clay surface (Gee et al. 1992). DSC provided further information about the energy state of water in the Ca- and HDTMA-exchanged clay sam-

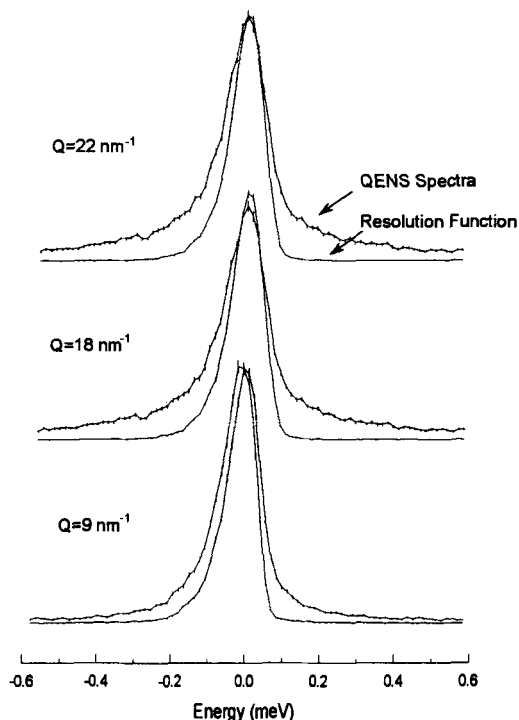


Figure 1. Quasi-elastic incoherent neutron spectra and resolution function for Ca-bentonite at 0.1 g H<sub>2</sub>O g<sup>-1</sup> dry weight clay at 3 values of momentum transfer ( $Q$ ). Error bars represent standard deviation about measured intensity for each value of energy transfer.

ples. DSC analyses were conducted using a DuPont 9000 DSC. Approximately 10 mg of clay were placed in platinum sample boats, and heated from 25–250° under N<sub>2</sub> at a heating rate of 10° min<sup>-1</sup>.

## RESULTS

### QENS

Figure 1 shows QENS spectra for the Ca-saturated sample at 10% water content for 3 different momentum transfer values ( $Q = 9, 18$  and  $22 \text{ nm}^{-1}$ ). The solid line is the resolution function for the spectrometer and shows the intensity of scattered neutrons from the clay sample in the absence of diffusive motion. This increases smoothly from energy transfers of about  $-0.2 \text{ meV}$  to reach a maximum value near  $0 \text{ meV}$  before returning to minimal scattering intensity beyond about  $+0.1 \text{ meV}$ . The scattering at  $25^\circ \text{C}$ , which includes the broadening arising from the diffusive motion of water (dashed line), takes place over a much wider range in energy transfer values (with statistically significant scattering at  $\pm 0.6 \text{ meV}$ ). Scattering at different momentum transfer values  $Q$  probe proton motion over different length scales; low  $Q$  corresponds to large displacements (such as translational motion), while increasing  $Q$  probes shorter length scales of motion (such as rotational and translational motion).

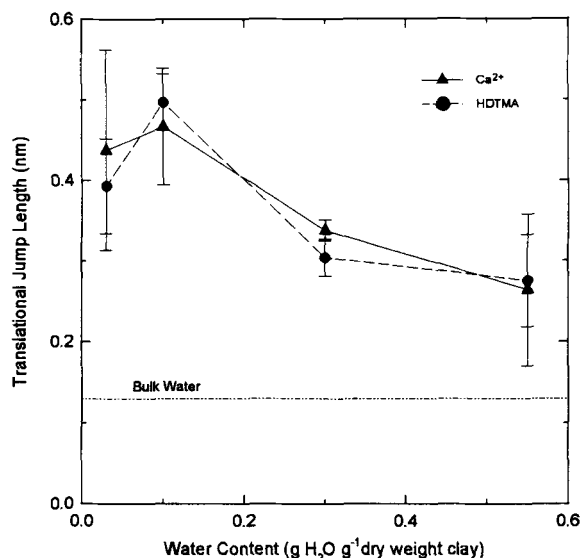


Figure 2. Translational jump length versus water content for Ca- and HDTMA-exchanged clay.

A preliminary experiment was conducted to evaluate the quasi-elastic scattering due to proton motion associated with the HDTMA in the samples. Spectra obtained for an HDTMA-clay sample at  $\sim 23^\circ \text{C}$ , which had previously been dehydrated by heating to  $110^\circ \text{C}$  under vacuum ( $10^{-5} \text{ Torr}$ ) for 4 h, were essentially superimposable upon the resolution function (HDTMA-clay at 15 K). These results indicate negligible quasi-elastic scattering due to HDTMA motion over the length and time scales probed by the spectrometer; its large mass relative to water and structural and steric factors apparently limited translational and rotational motion of the HDTMA within the interlayer such that effectively all quasi-elastic broadening in HDTMA-clay samples with water added could be attributed to motion of water.

Fitting Equations [1–3] to data like that shown in Figure 1 yielded estimates of mean jump length for Ca- and HDTMA-exchanged clays at varying water contents (Figure 2). Jump lengths were similar for both clays at equivalent water contents and generally decreased with increasing water contents, from fitted values of  $0.4\text{--}0.5 \text{ nm}$  at the low water contents ( $\sim 0.03\text{--}0.1 \text{ g H}_2\text{O g}^{-1} \text{ d.w. clay}$ ), to  $\sim 0.27 \text{ nm}$  at about  $0.55 \text{ g H}_2\text{O g}^{-1} \text{ d.w. clay}$ . Notably, over this water content range which spans sub-monolayer coverage to 2–3 layers of water, the mean jump length remains significantly higher than that for bulk water ( $\sim 0.13 \text{ nm}$ ). Error bars in Figure 2 (and subsequent figures) correspond to 1 standard deviation about mean values from measurements of duplicate samples and multiple numerical fits of data to the scattering law. Deviation was large at both the lowest and highest water contents. At the lowest water content, the fit of the model

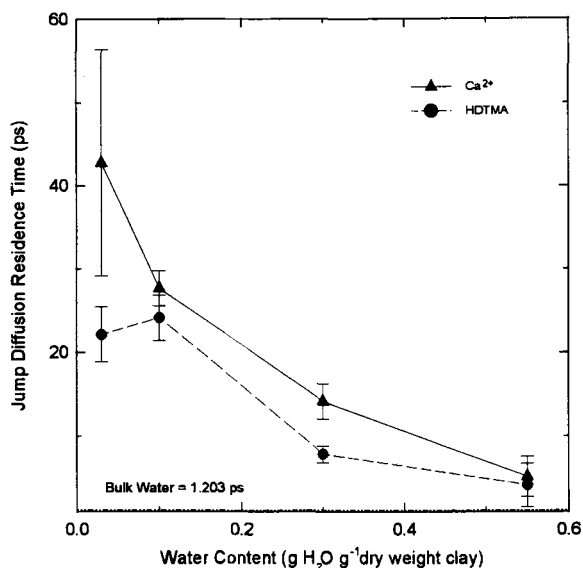


Figure 3. Jump diffusion residence time versus water content for Ca- and HDTMA-exchanged clay.

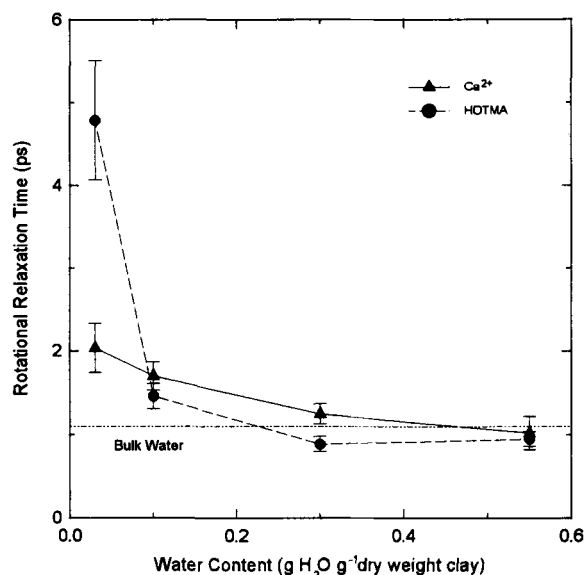


Figure 4. Rotational relaxation time versus water content for Ca- and HDTMA-exchanged clay.

of Teixeira et al. (1985) (Equations [1–3]) to the experimental data was comparatively poorer than at higher water contents. Sample variability and possible multiple scattering for one of the duplicate samples contributed to the variability at the highest water content.

Jump diffusion residence times in the clays were markedly longer than that of bulk water and, like jump lengths, tended to decrease with increasing water contents for the 2 different cation saturations (Figure 3). While the measured jump lengths were quite similar for the 2 cations (Figure 2), jump diffusion residence times for the HDTMA-saturated clays were lower than that for the Ca-clay at equivalent water contents (Figure 3). At the lowest water content, a mean jump diffusion residence time of 43 ps was estimated for the Ca-clay, a value about 35 times higher than that for bulk water. At the equivalent water content, the residence time for the HDTMA-clay was estimated to be about 22 ps (Figure 3). Increasing water content to about 0.1 g g<sup>-1</sup> d.w. resulted in a decrease in the jump diffusion residence time for the Ca-clay and a slight increase for the HDTMA-clay to a mean value of about 24 ps. Increasing water content resulted in further reductions in jump diffusion residence times, although residence times remained above that for bulk water (Figure 3).

Rotational relaxation times of water were comparatively less affected by the clay surface than the other parameters (Figure 4). Rotational relaxation times were quite similar to that of bulk water at the 2 highest water contents for both clays. At the lowest water content, the rotational relaxation time of the water in the

HDTMA-clay was about 4 times that of bulk water and twice that of the Ca-clay (Figure 4).

#### XRD

The *d*-values of the bentonite increased with increasing water content as noted by numerous other researchers. The *d*-values increased approximately linearly with increasing water content in the Ca-saturated clay from 1.2 nm at ~0.03 g g<sup>-1</sup> d.w. to approximately 1.8 nm at ~0.55 g g<sup>-1</sup> d.w. (Figure 5). (At this highest water content, a somewhat weaker 1.55-nm reflection

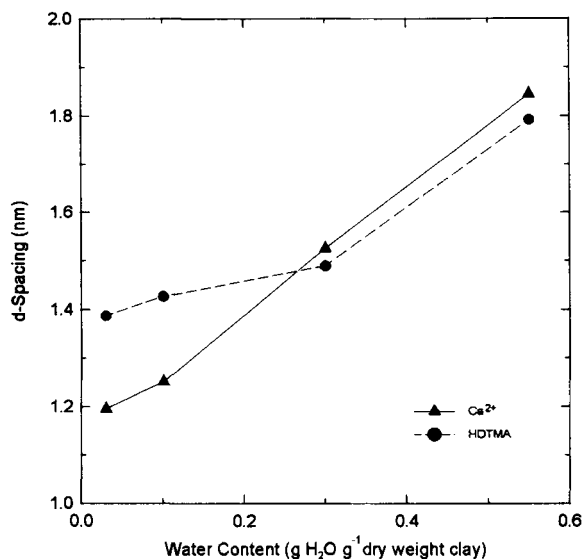


Figure 5. Basal spacing versus water content for Ca- and HDTMA-exchanged clay.

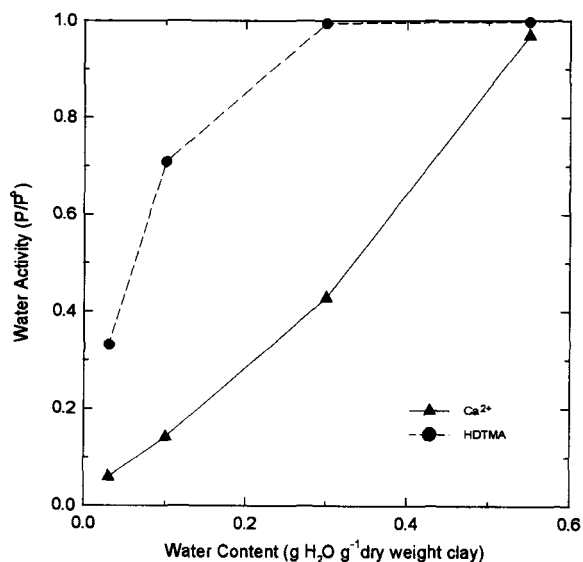


Figure 6. Water activity versus water content for Ca- and HDTMA-exchanged clay.

was also present.) HDTMA-clay was propped open at the lowest water content an additional 0.2 nm as compared with the Ca-clay. The  $d$ -values increased modestly with increasing water contents to  $\sim 0.3 \text{ g g}^{-1}$  d.w., and then increased more dramatically at  $0.55 \text{ g g}^{-1}$  d.w. (Figure 5) to yield a single, well-defined reflection corresponding to an  $\sim 1.8 \text{ nm}$   $d$ -value.

#### Water Activity

Water activity, measured as a vapor pressure normalized against the saturation vapor pressure of water, differed markedly between the 2 samples at a given gravimetric water content (Figure 6). Water activity in the Ca-clay increased approximately linearly with increasing water content, from about 0.06 at  $0.03 \text{ g g}^{-1}$  d.w. to  $\sim 0.98$  at  $0.55 \text{ g g}^{-1}$  d.w. The water activity of the HDTMA-clay was 2–5 times higher than that of the Ca-clay at the equivalent water contents at all but the highest water content (Figure 6), where the HDTMA sample bore a water activity essentially that of bulk liquid water ( $>0.99$ ).

The potential of water is related to its activity ( $a_w$ ) through:

$$\psi = \frac{RT}{M} \ln a_w \quad [5]$$

where  $\psi$  is the water potential (J/kg),  $R$  is the gas constant,  $T$  is temperature (K) and  $M$  is the molecular weight of water (Rawlins and Campbell 1986). Thus, a very wide range of potentials exists over the water content range evaluated in this study ( $\sim 0$  to  $-1000$  bars).

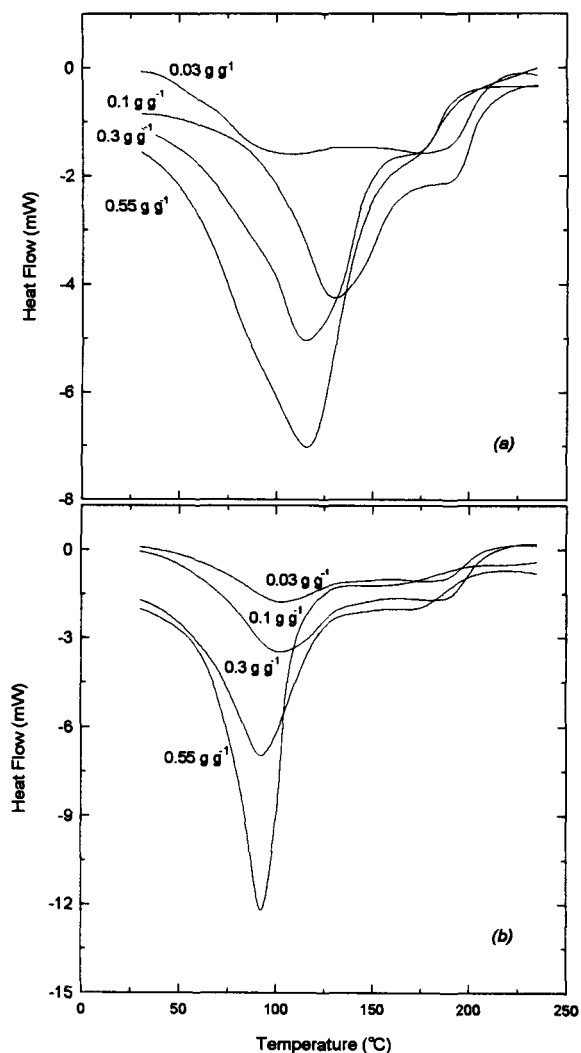


Figure 7. Differential scanning calorimetry results for a) Ca- and b) HDTMA-exchanged clay.

#### DSC

DSC provided additional information about the differences in the energy states of water for the 2 different exchange phase saturations (Figures 7a and 7b). For the Ca-clay at the lowest water content, a broad endotherm with shoulders centered at approximately 100 and 170 °C was found. Ca-clay at a water content of  $0.1 \text{ g g}^{-1}$  d.w. was found to have a well-developed endotherm centered at about 135 °C, with the shoulder centered at 170 °C still relatively well defined. With increasing water contents ( $0.3$  and  $0.55 \text{ g g}^{-1}$  d.w.), the endotherm associated with the first dehydration step increased in area and decreased in temperature, approaching that of bulk water at the highest water content (Figure 7a).

In contrast with those for the Ca-clay, the endotherms for the HDTMA-clay were typically sharper,

especially at the higher water contents, and more importantly occurred at lower temperatures at any given water content as compared to the Ca-clay (Figures 7a and 7b). For example, at 0.3 g H<sub>2</sub>O g<sup>-1</sup> d.w. clay, the endotherm for dehydration of the Ca-clay was approximately symmetrical, with a width at half-maximum of about 65 °C, and centered at approximately 115 °C. Conversely, the endotherm for dehydration of the HDTMA-clay was not as symmetrical, being sharper on the rising limb, bore a lower width at half-maximum (~40 °C), and was centered at about 95 °C (lower than that which would be expected for bulk liquid water). These differences between the 2 exchange phase saturations are even more pronounced at the highest water content. A general conclusion, consistent with the water activity measurements, is that the energy state of water, at an equivalent water content, is markedly different for the Ca- and HDTMA-saturated clays.

### DISCUSSION

The results of the neutron scattering experiments indicate that the translational mobility of water in Ca- and HDTMA-exchanged bentonite is quite different compared to that of bulk water. Jump diffusion residence times for both the Ca- and HDTMA-exchanged clays were 3 to 20–30 times longer than that for bulk liquid water (Figure 3). Translational jump diffusion lengths for both clays were also larger (by a factor of ~2–4) than that of bulk water (Figure 2). Except at the lowest water contents, rotational mobility for the 2 clays were comparable and not substantially altered relative to bulk water, however (Figure 4).

The results of the present study are in general agreement with those reported by other researchers. Cebula et al. (1981) reported translational jump lengths of  $0.32 \pm 0.20$ ,  $0.39 \pm 0.20$  and  $0.37 \pm 0.20$  nm for Li-saturated montmorillonite at water activities of 0.32, 0.58 and 0.98, respectively. The relatively large uncertainties in their fitted jump lengths may obscure the trend of decreasing jump length with increasing water content found in the present study, but their findings are within the range of jump lengths reported here (0.26–0.47 nm for Ca-clay). The translational residence times reported by Cebula et al. (1981) for water in the Li-montmorillonite decreased with increasing water activity, from  $43 \pm 5$  to  $33 \pm 5$  to  $23 \pm 5$  ps, which are somewhat higher than the residence times found here for Ca-clay at similar water activities (Figure 3). Hall et al. (1978), in a preliminary analysis of water in Ca-montmorillonite, reported broad components to the QENS spectra for 2- and 3-layer hydrates of Ca-montmorillonite which yielded fitted diffusion coefficients of 13.7 and  $16.0 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup>, in good agreement with the translational diffusion coefficient of  $13.6 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup> measured in our study for Ca-clay at 0.3 g g<sup>-1</sup> d.w.. However, they also reported a

narrow component observed with a high-resolution spectrometer to which they attributed translational diffusion with a magnitude of  $3.4 \times 10^{10}$  m<sup>2</sup> s<sup>-1</sup>, lower than the values found in our study and those reported by Cebula et al. (1981). More detailed analysis of the data of Hall et al. (1978) is necessary before their findings can be fully evaluated, however (Cebula et al. 1981).

The reported jump lengths and relaxation times are, of course, strongly dependent upon the assumptions of the model used. In their studies of water in the interlayer of clays, both Cebula et al. (1981) and Hall et al. (1978) evaluated possible anisotropies with respect to translational motion within the interlamellar spaces of the clay and concluded that a fully isotropic model (on the length scale probed by the neutrons) adequately described the data. The QENS spectrometer samples a Q-range which corresponds to a length-scale roughly about 0.1–1 nm, that is, generally less than or on the order of the interlayer spacing of our clays. Furthermore, disordered powders were used in our study, which would randomize the orientation of the interlayers and remove any differentiable anisotropy from the QENS spectra (although some modest orientation was incurred for the highest water content samples). Based on these factors, then, application of an isotropic model for translation is considered justified (Hall et al. 1978; Cebula et al. 1981).

The XRD results at the lowest water contents reveal different interlayer spacings for the 2 clays, with the HDTMA-clay propped open an additional 0.2 nm as compared to the Ca-clay. Alkylammonium cations have been used to evaluate the layer charge of 2:1 expandable minerals (Lagaly and Weiss 1969; Lagaly 1981; Senkayi et al. 1985). A *d*-value of 1.4 nm corresponds to approximately monolayer coverage by the HDTMA and suggests low layer charge for the clay used in this study; this contradicts, however, the rather high CEC measured for the clay (102 cmol(+) kg<sup>-1</sup>). It was noted that the HDTMA solution following the approximately 1-h equilibration with the clay remained foamy, suggesting incomplete exchange. Based on data relating surface tension to HDTMA concentrations, the measured surface tension of the supernatant following dilution and an exchange capacity of 102 cmol(+) kg<sup>-1</sup>, we have estimated that the clay was 60–80% saturated with HDTMA.

DSC and water activity measurements demonstrate rather significant energy differences for water in the Ca- and HDTMA-clays as compared to that of bulk liquid water. The energy state of water, measured both as *P/P*<sup>0</sup> and given by the temperature for dehydration based on DSC, decreased with increasing water content. An additional and important observation is that, in contrast with measured mobilities which differed modestly with exchange phase saturation, the energy state at a given water content was markedly different

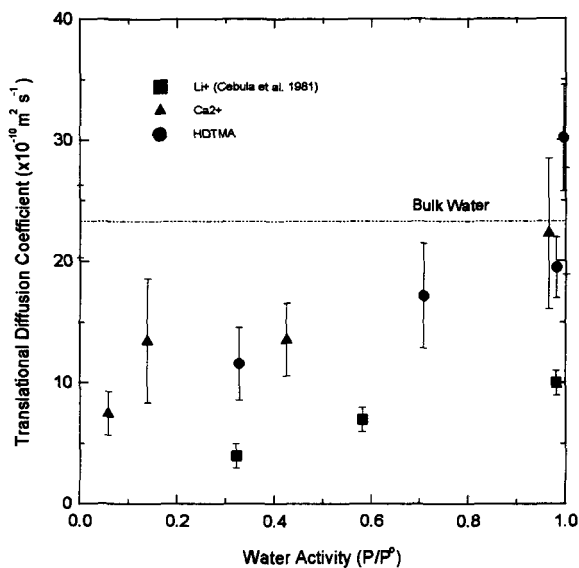


Figure 8. Translational diffusion coefficient versus water activity for Ca- and HDTMA-exchanged clay. Results from Cebula et al. (1981) for Li-montmorillonite are included.

for the Ca- and HDTMA-clay (Figures 6, 7). A plot of translational diffusion coefficient versus  $P/P^0$  (Figure 8) yielded a straight line with an  $r$  of 0.88 and intercept at  $P/P^0$  of 1.0 equal to  $23.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ , in good agreement with our measured translational diffusion coefficient of bulk water at room temperature of  $23.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  and the bulk value reported by Teixeira et al. (1978) of  $22.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . Interestingly, the highest water content HDTMA-clay sample yielded a translational diffusion coefficient approximately 30% higher than that for bulk water. It appears that the HDTMA perturbs the hydrogen-bonding network of water within the clay sufficiently to increase water mobility relative to that in the bulk. Included on Figure 8 are the results for Li-montmorillonite (Cebula et al. 1981), which also suggest a linear increase in the translational diffusion coefficient with increasing water activity. However, the magnitude of the diffusion coefficients for the Li-clay were about one-third to one-half that for the Ca- and HDTMA-clays at comparable water activities.

The picture that emerges from the results of this study, which is consistent with other findings, is that water in clays bears a translational mobility and energy state lower than that of bulk water. While measurements have been previously made on alkali and alkaline earth-exchanged smectites, we believe these are the first reported measurements for clay exchanged with alkylammonium cations. An important conclusion, based on our data comparing Ca- and HDTMA-exchanged bentonites, is that the translational diffusion coefficient of water appears to be related to water activity, and not uniquely influenced by the specific type

of counterion present. Further work is needed to confirm this observation, however.

## ACKNOWLEDGMENTS

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