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AN FTIR STUDY OF WATER SORPTION ON TMA- AND TMPA-MONTMORILLONITES

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Abstract—Water inhibits sorption of uncharged organic compounds on montmorillonites saturated with small alkylammonium cations such as tetramethylammonium (TMA) and trimethylphenylammonium (TMPA). As a first step toward understanding the mechanism by which water inhibits arene sorption on TMA- and TMPA-montmorillonites, infrared spectroscopy and water sorption isotherm experiments were conducted to determine whether water preferentially hydrates adsorbed TMA and TMPA cations rather than the siloxane surface. Infrared spectra of normal-charge and reduced-charge TMA- and TMPA-montmorillonites were obtained at partial water vapor pressures from 0.075 to 0.92 to determine if water vapor hydrates the adsorbed cations. Water adsorbed at partial pressures from 0 to about 0.2 caused the wavenumber position of the HOH deformation vibration of adsorbed water to shift 4 to 10 cm^{-1} to higher wavenumber and the methyl deformation vibrations of adsorbed TMA and TMPA cations to shift 1 to 2 cm^{-1} to higher wavenumber, providing evidence that water interacts directly with adsorbed TMA and TMPA ions. There were no shifts in the ring stretching or C-H out-of-plane vibrations of TMPA, which indicates that water interacts with the methyl groups of TMPA, not with TMPA's aromatic ring. Water vapor sorption isotherms showed that normal-charge montmorillonites adsorb more water than do reduced-charge montmorillonites, consistent with the higher concentration of adsorbed cations on normal-charge clay. More water was adsorbed by TMA-montmorillonite than by TMPA-montmorillonite, consistent with the higher hydration energy of TMA. Thus, both the infrared and sorption isotherm results show that water preferentially hydrates adsorbed TMA and TMPA, not the siloxane surface of montmorillonite.

Key Words—FTIR, TMA-montmorillonites, TMPA-montmorillonites, Water Sorption.

INTRODUCTION

When small organic cations such as TMA or TMPA occupy exchange sites on montmorillonite, the interlayer siloxane surface becomes accessible to nonpolar molecules such as N_2 or benzene (Barrer and Reay 1957; Barrer and Perry 1961; Clementz and Mortland 1974; Lee et al. 1990; Jaynes and Boyd 1991; Stevens and Anderson 1996a). Lee et al. (1990) proposed that water inhibits arene sorption on TMA-montmorillonites by solvating either the siloxane surface itself, the adsorbed TMA ions, or both, thereby decreasing the size of interlamellar pores. In subsequent research with TMPA-montmorillonites, Jaynes and Boyd (1991) concluded that the siloxane surface is hydrophobic and that arenes sorb onto the siloxane surface, though these authors did not directly address the question of whether water-surface interactions are stronger or weaker than are water-cation interactions. On TMA-montmorillonite, it is probable that water-TMA interactions are predominant since the hydration energy of TMA^+, 32 kcal mol^{-1} (Cotton and Wilkinson 1966) is similar to that of K^+ or NH_4^+, and water sorption isotherms for TMA-montmorillonite are similar to those for NH_4-montmorillonite (Gast and Mortland 1971). However, the low water solubility of TMPA suggests that TMPA may have very little affinity for water. Consequently, at very low water contents, it is possible that water may hydrate the siloxane surface rather than adsorbed TMPA ions.

Infrared spectroscopy has shown that interactions between adsorbed metal ions and water are more important than are interactions between water and the siloxane surface (Russell and Farmer 1964; Farmer and Russell 1971; Suquet et al. 1977; Sposito and Prost 1982; Poinsignon et al. 1978; Johnston et al. 1992). Inorganic cations polarize the OH bond of water molecules in the first coordination shell and cause the ν_2 (HOH deformation) band of water to shift to a lower frequency relative to bulk water. The shift is greatest for strongly hydrated cations with high charge and small radius. As the number of adsorbed water molecules per cation increases, the ν_2 peak position shifts to a higher wavenumber and ultimately reaches a plateau at which water-water interactions become dominant (Johnston et al. 1992). This plateau is reached when there are as few as 5 H_2O molecules per cation for large monovalent ions such as K^+, but 10 H_2O molecules per cation may be required for divalent ions such as Cu^{2+} or Co^{2+} (Johnston et al. 1992). That the position of the ν_2 band depends upon cation properties at low water contents is evidence that water adsorbed by montmorillonite interacts with adsorbed metal cations via ion-dipole interactions.

Studies of the OH (or OD) stretching region of water adsorbed on metal-ion-saturated clays have shown that water coordinated to metal ions also forms weak hydrogen bonds with uncharged siloxane oxygen atoms and somewhat stronger hydrogen bonds with siloxane oxygens near tetrahedral substitution sites

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Table 1. Properties of reduced-charge and normal-charge TMA- and TMPA-montmorillonites.

Treatment	d(001) (Å)	N_2 surface area[2] ($m^2\ g^{-1}$)	Total C[3] ($g\ kg^{-1}$)	Adsorbed cation[4] ($mmol\ kg^{-1}$)
Reduced-charge TMA	13.6	289 ± 30	27.7 ± 0.7	474 ± 14
Normal-charge TMA	13.6	202 ± 26	40.7 ± 0.3	847 ± 6
Reduced-charge TMPA	13.6[1]	318 ± 14	48.6 ± 0.9	449 ± 8
Normal-charge TMPA	15.0[1]	252 ± 28	88.1 ± 1.0	814 ± 11

[1] Obtained from Fourier transform of XRD data (Stevens and Anderson 1996).
[2] Avg ± SD (N = 2 or 3) from three-point BET N_2 adsorption isotherms using a Quantachrome Quantasorb Jr. surface area analyzer.
[3] Avg ± SD (N = 2) of total C determined by combustion at 900°C using a Dohrmann DC-190 high-temperature carbon analyzer.
[4] Avg ± SD (N = 2) calculated with the equation: Adsorbed cation = total g C/kg clay × mmol cation/g C in cation.

(Farmer and Russell 1971). Thus, hydrogen bonding between surface oxygens and adsorbed water occurs in conjunction, not in competition, with hydration of adsorbed metal ions; cation hydration is more important than surface hydration, at least when inorganic cations are adsorbed.

This paper describes a combination of spectroscopic and macroscopic experiments to test the hypothesis that water adsorbed at low water contents on TMA- and TMPA-montmorillonites hydrates these organic cations, not the siloxane surface. Normal-charge and reduced-charge Wyoming montmorillonites were used to provide different adsorbed cation concentrations and different accessible siloxane surface areas. Water vapor sorption isotherms were obtained to determine the number of adsorbed water molecules per cation at a given partial pressure of water and to determine whether more water was adsorbed on normal-charge or reduced-charge clay. Greater water sorption on normal-charge than reduced-charge clay at given P/P_0 would suggest that the quaternary alkylammonium ions, not the siloxane oxygens, are the preferred water sorption site, though macroscopic data alone cannot give conclusive information about sorption mechanisms. Infrared spectroscopy was used to probe water-cation interactions at the molecular level. The position of the water deformation band, the methyl deformation vibrations of TMA, and the methyl deformation and ring vibrations of TMPA were measured as a function of partial water pressure to determine whether water hydrates these adsorbed organic cations. Information about the effect of water adsorption on the vibrations of adsorbed alkylammonium ions is essential if one is to use infrared spectroscopy to study competitive sorption of water and organic pollutants on organoclays, which is the focus of a related study (Stevens et al. 1996b).

MATERIALS AND METHODS

Organoclay Preparation

Wyoming montmorillonite (SWy-1) was obtained from the Clay Minerals Society Source Clays Repository at the University of Missouri-Columbia. The <2-μm fraction was separated from coarser material by sedimentation and saturated with either LiCl or NaCl as described previously (Stevens and Anderson 1996a). Reduced-charge clay was prepared using a method similar to that described by Brindley and Ertem (1971). Briefly, a dialyzed Na-montmorillonite suspension was mixed with a Li-montmorillonite suspension to give a 50:50 mixture of Li-montmorillonite and Na-montmorillonite. This mixture was freeze-dried and heated to 250°C. The collapsed, reduced-charge clay was re-expanded by sonicating 2-g subsamples of clay in 200 ml of a 70% methanol-water mixture for 20 min in an ice-water bath (Greene-Kelly 1953; Brindley and Ertem 1971; Jaynes and Bigham 1987).

To prepare TMA- and TMPA-montmorillonites, TMA chloride (four times the CEC) and TMPA bromide (ten times the CEC) were added to normal-charge and reduced-charge montmorillonites in 70% methanol-water suspensions and stirred for 72 h. The clays then were dialyzed until halide-free and were freeze-dried. To improve the homogeneity of the clays, each freeze-dried clay (normal- or reduced-charge, TMA- or TMPA-saturated) was mixed gently in a mortar and pestle. Selected properties of the clays are reported in Table 1.

Water Vapor Sorption Isotherms

Between 200 and 500 mg of each of the four freeze-dried, homogenized clays (dried at 80°C and stored over P_2O_5 in a desiccator) was placed in the sample holders of a McBain balance (Figure 1; McBain and Bakr 1926). The sample chambers were evacuated and then heated to 80°C for 72 h to remove any water that may have adsorbed on the clays when they were transferred from the desiccator to the balance. No decomposition of alkylammonium montmorillonites occurs at temperatures up to 105°C (Gast and Mortland 1971). After the heat and vacuum treatment, the clay samples were equilibrated at 23.5 ± 0.5°C with water vapor at absolute pressures ranging from 0.90 to 17.25 torr. After one hour of equilibration at each pressure, the manometer reading, temperature, and spring displace-

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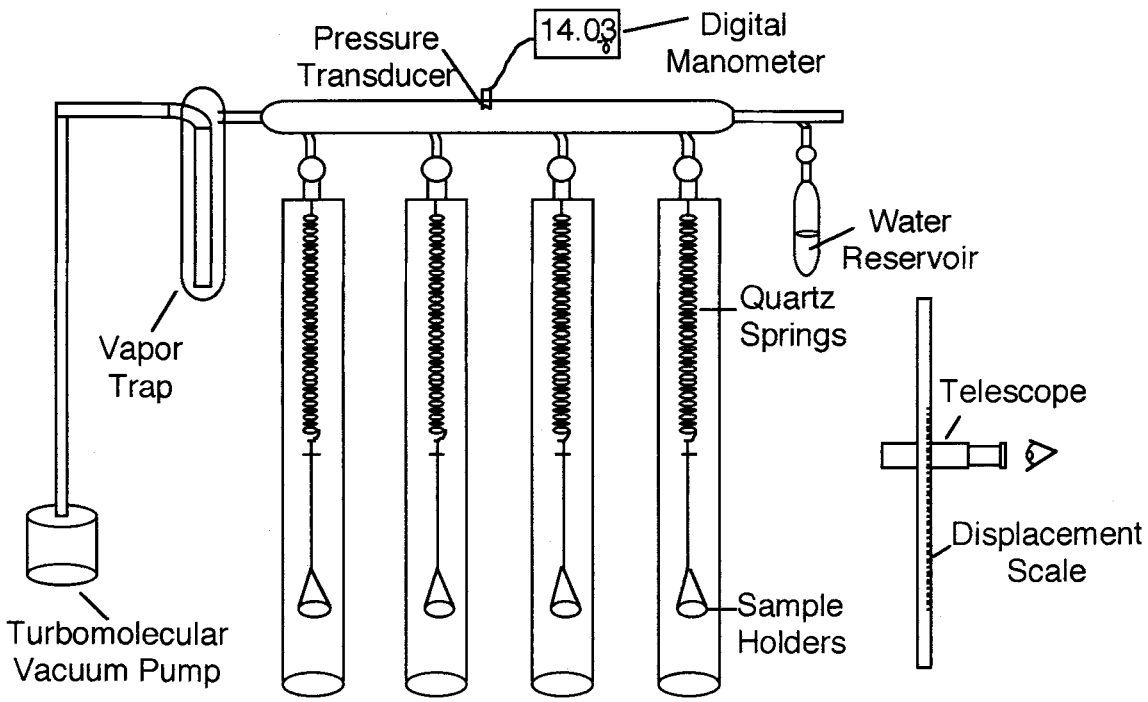


Figure 1. Diagram of the McBain balance used to collect water vapor sorption isotherms on TMA- and TMPA-saturated montmorillonites. Water vapor pressure is controlled by releasing water vapor from the sorbate reservoir into vacuum. Mass of adsorbed water is determined by measuring the displacement of quartz springs attached to sample holders.

ments were recorded. Isotherms were collected in the adsorption direction. Mooney et al. (1952) reported that adsorption isotherms for montmorillonites saturated with inorganic cations depended on initial water content, but the low hydration energies of TMA and TMPA should minimize this problem for the clays used in this study. Further, all of the samples used in this study started at the same initial water content (vacuum-dried over P_2O_5) and were treated identically. Thus, adsorption isotherms are satisfactory for our goal of comparing water sorption by normal- and reduced-charge TMA- and TMPA-montmorillonites. Water sorption data for each of the two charge treatments and two organic cations were collected simultaneously.

Infrared Spectroscopy

Infrared spectra of normal-charge and reduced-charge TMA- and TMPA-montmorillonites were obtained at partial water pressures from 0 to 0.72. Spectra were collected first using clay films supported on AgCl disks. To verify that the peak positions were reproducible and independent of the method used to prepare the clay films, spectra of self-supporting films of reduced-charge TMA- and TMPA-montmorillonites were collected at selected P/P_0 values.

To prepare disk-supported films, 70 mg each of normal- and reduced-charge TMA- and TMPA-montmorillonites were suspended in 10 ml of methanol and sonicated for three 10-min intervals in an ice-water bath. After the third sonication, coarse material was allowed to settle for about 30 min and 1-ml aliquots of the remaining clay suspensions were pipetted onto 13-mm diameter Delrin™ AgCl disks (E.I. duPont de Nemours®). It was necessary to repeat the pipetting several times to obtain a sufficiently thick film, defined as a film for which the clay O-H stretching vibration at 3650 cm^{-1} was approximately 20% transmittance. The amount of clay on the disks was 0.8 ± 0.15 mg cm^{-2}.

Self-supporting films were prepared by pipetting aqueous suspensions of normal-charge and reduced-charge Na-montmorillonite onto glass microscope slides. After the clay films dried, each film was reacted overnight at 60°C with 20 mL of a 5 mM solution of either TMA chloride or TMPA bromide in ethanol. Excess solution was removed, and the films were washed with 10 mL of ethanol to remove any excess salts. The TMA- and TMPA-montmorillonite films were allowed to dry. A razor blade was used to remove the films from the slides. The density of the self-supporting clay films was about 1 g cm^{-2}.

Clay films were placed in an infrared cell (Figure 2) that contained salt solutions (Weast 1986) to control relative humidity. The intensity of the OH stretching peak of adsorbed water (3000 to 3600 cm^{-1}) was mon-

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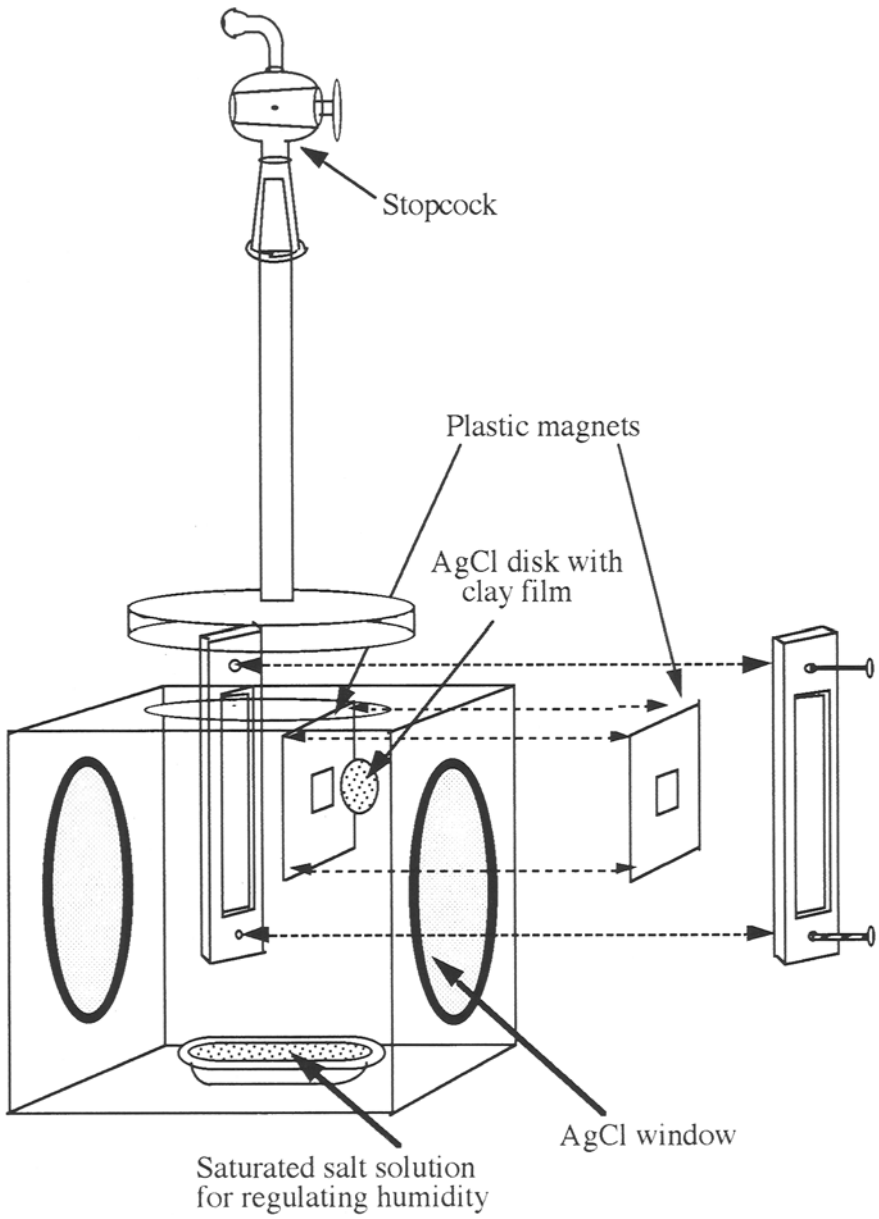


Figure 2. Diagram of controlled-atmosphere FTIR cell used to equilibrate TMA- and TMPA-saturated smectites with water vapor and to collect spectra of clay-water complexes.

itored until the peak intensity was constant with time, which typically required 1.5 to 2 h. Single-beam spectra of disk-supported films were collected using a Perkin-Elmer 1600 FTIR spectrometer with a DTGS detector, 2 cm^{-1} resolution, no apodisation, and 50 to 75 scans. Background spectra were taken of a clean AgCl disk placed in the sample holder over appropriate salt solutions in the IR cell. Single-beam spectra of self-supporting films were collected using a Perkin-Elmer 1710 spectrometer with a DTGS detector 2 cm^{-1} resolution, no apodisation, and 75 scans. Background spectra for the self-supporting films were recorded without the clay film in the cell.

Single-beam spectra were imported into the MS-DOS program SpectraCalc® (Galactic Software Inc.) and transformed into absorbance units. Spectra were smoothed using an 11-point Savitsky-Golay procedure. The baseline was leveled along six or seven baseline points in the spectrum, then zeroed. Peak positions were determined either by the location of the peak maximum or by calculating the center of mass using the wavenumber as the position vector and the

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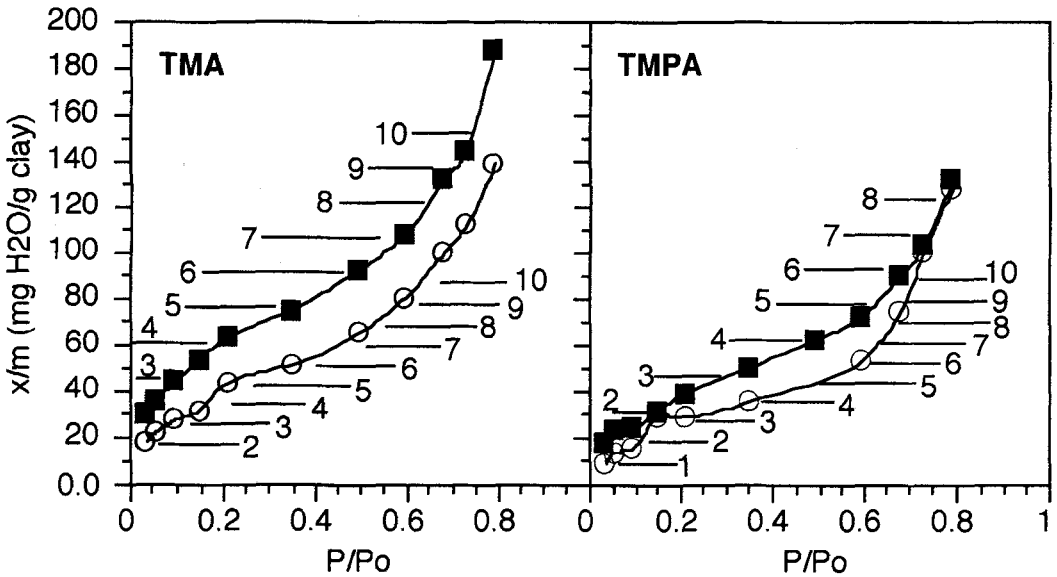


Figure 3. Water vapor sorption isotherms on normal-charge (■) and reduced-charge (○) TMA- and TMPA-montmorillonites. Number of water molecules sorbed per cation is indicated with horizontal lines at appropriate x/m values. a) TMA-montmorillonite; b) TMPA-montmorillonite.

incremental peak intensities as the mass vector. Center-of-mass calculations allow peak positions to be determined to better than instrumental resolution if individual peaks can be resolved (Griffiths and De Haseth 1986). Peak maxima locations were used for TMPA methyl asymmetric deformation and ring stretching vibrations because these two peaks overlapped slightly with one another. The uncertainty of peak maxima estimates is about 2 cm^{-1}, which is the limit of instrument resolution. Center-of-mass estimates were used for ν_2 HOH deformation bands of adsorbed water, TMA methyl deformation bands and TMPA C-H out-of-plane vibrations because no other peaks overlapped with these peaks.

RESULTS AND DISCUSSION

Water Sorption Isotherms

Water vapor adsorption isotherms for TMA-montmorillonites (Figure 3a) and TMPA-montmorillonites (Figure 3b) show that normal-charge clays, which have higher adsorbed cation concentrations, adsorb more water vapor than do reduced-charge clays. Greater water sorption on normal-charge than reduced-charge clays suggest that the cation, not the siloxane surface, is the preferred site of water sorption on clays saturated with TMA and TMPA. If water were to solvate the siloxane surface in preference to the adsorbed cations, greater sorption would have occurred on the reduced-charge clays, which have greater N_2-surface areas than do normal-charge clays (Table 1). Greater water sorption on normal-charge clays at low P/P_0 supports the conclusion of Jaynes and Boyd (1991) that uncharged siloxane surfaces are more hydrophobic than are TMPA cations.

Although the total amount of adsorbed water is greater for normal-charge than reduced-charge TMA- and TMPA-montmorillonites, reduced-charge clays sorb at least one more water molecule per cation than do their normal-charge counterparts at P/P_0 greater than 0.2 (Figure 3). Close proximity of adjacent cations on normal-charge clays may sterically restrict the number of water molecules in cation hydration shells. This apparently is especially true for TMPA montmorillonite: at P/P_0 greater than 0.7, normal-charge TMPA-montmorillonite sorbed only slightly more water than did reduced-charge TMPA-montmorillonite, and there were three more water molecules per cation on reduced-charge than normal-charge TMPA-montmorillonite, apparently because the size of the TMPA hydration shell was more restricted sterically on normal-charge montmorillonite.

More water was adsorbed by TMA-montmorillonites than by TMPA-montmorillonites (Figures 3a and 3b). This result indicates that TMA-montmorillonites are more hydrophilic than are TMPA-montmorillonites, in part because the hydration energy of TMA probably is greater than that of TMPA. In addition, the bulky phenyl group, which occupies more siloxane surface than does a methyl group, may sterically restrict the number of water molecules in the TMPA hydration shell, as mentioned above. The amount of water sorbed by TMA-montmorillonite in this study was greater than that reported by Gast and Mortland (1971), possibly because they used saturated salt so-

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lutions to control the partial pressure of water vapor in a system of one atmosphere total pressure, whereas the present study was conducted under partial vacuum, with the vapor pressure of water equal to the total pressure in the sample chamber.

The isotherm shapes (Figures 3a and 3b) were similar to those obtained by Gast and Mortland (1971) for TMA-smectites. The steep slope at high P/P_0 might suggest that condensation begins to occur when greater than 6 H_2O per cation are adsorbed. Condensation would likely occur on external surfaces of these clays, because X-ray diffraction measurements at $P/P_0 = 1.0$ showed little interlayer expansion (data not shown). Furthermore, Johnston et al. (1992) found evidence that multilayer water sorption occurs on external siloxane surfaces.

Infrared Spectroscopy

WATER DEFORMATION VIBRATION. Typical FTIR spectra of each clay at several partial water pressures are shown in Figure 4. The positions of the HOH deformation vibration (ν_2) of adsorbed water (near 1630 cm^{-1}) are plotted in Figure 5 for $P/P_0 > 0.15$. For P/P_0 less than 0.15, the ν_2 peak of adsorbed water barely rose above the baseline and was so broad (Figure 4) that its wavenumber position could not be determined reliably by either center-of-mass or peak-maxima methods.

On TMA-montmorillonite, the water ν_2 band moved about 4 to 6 cm^{-1} to higher wavenumber as P/P_0 increased from 0.15 to 0.72. There is little difference between normal- and reduced-charge TMA-montmorillonites over the range of P/P_0 values for which we have data (Figure 5). The water ν_2 peak position appears to reach a plateau at about 6 water molecules per cation, estimated from water vapor sorption isotherms, for both the normal-charge and reduced-charge TMA montmorillonites.

On TMPA-montmorillonite, the water ν_2 peak position increased about 8 to 10 cm^{-1} with increasing P/P_0 (Figure 5). There is little difference between the normal-charge and reduced-charge TMPA-montmorillonites, similar to the results for TMA-montmorillonite. Although there is scatter in the plots of ν_2 position vs. P/P_0, the consistent upward trend at low P/P_0 for normal-charge and reduced-charge TMA- and TMPA-montmorillonites suggests that water interacts directly with the adsorbed organic cations. Further evidence is provided by the methyl deformation vibrations of TMA and TMPA, which are described in the next section.

Previous research (Johnston et al. 1992 and references cited therein) has shown that the increase in ν_2 wavenumber with increasing P/P_0 is greatest for cations with high ionic potential. Although TMA is more strongly hydrated and has a higher ionic potential than TMPA, the ν_2 wavenumber position for adsorbed water increased more on TMPA-montmorillonites than on TMA-montmorillonites. An explanation for this apparent discrepancy is that most of the increase in ν_2 peak position on TMPA-montmorillonite occurred with less than four H_2O per cation (Figure 5), whereas on TMA-montmorillonite there were already almost four H_2O per cation at the lowest partial pressure at which the ν_2 position could be determined reliably. If we had been able to determine the ν_2 position accurately at lower P/P_0, perhaps by using a vacuum system similar to that described by Johnston et al. (1992), we likely would have been able to observe a larger increase in the ν_2 wavenumber of water adsorbed on TMA-montmorillonite.

CATION VIBRATIONS. Previous research has shown that the methyl asymmetric and symmetric vibrations of TMA are sensitive to their surrounding environment (Bottger and Geddes 1965). For TMA-montmorillonite, the methyl asymmetric deformation vibration (δ_a) is a narrow peak near 1485 cm^{-1} (Figure 4). For TMPA-montmorillonite, the methyl δ_a ($\approx$1490 cm^{-1}) and the ν_{19a} ring stretching ($\approx$1496 cm^{-1}) vibrations of TMPA overlap, but it is possible to resolve the two peaks (Figure 4).

For both normal-charge and reduced-charge TMA-montmorillonite, the wavenumber position of the methyl δ_a vibration of adsorbed TMA ($\approx$1485 cm^{-1}) gradually shifted by about 1 cm^{-1} to a higher frequency as P/P_0 increased from 0 to about 0.17, or as the number of water molecules per cation increased from 0 to 4 or 5 (Figure 6). The methyl symmetric vibration ($\approx$1419 cm^{-1}) is weakly absorbing, so its position could not be determined as accurately as that of the asymmetric vibration. Nevertheless, the methyl symmetric deformation peak of TMA shifted by about 1 cm^{-1} as P/P_0 increased to 0.2 (data not shown). Although shifts in the methyl asymmetric and symmetric deformation vibrations are small, the fact that water adsorption caused wavenumber shifts in both of TMA's methyl deformation vibrations and in the ν_2 vibration of adsorbed water on both normal-charge and reduced-charge TMA-montmorillonite is evidence that water hydrates adsorbed TMA ions at low water contents. Fripiat et al. (1969) did not observe any water-induced shifts in methyl deformation vibrations of mono- and dimethylammonium montmorillonites because adsorbed water formed by hydrogen bonds with NH protons and did not interact directly with the methyl groups. By contrast, water that hydrates adsorbed TMA ions must be in van der Waals' contact with the methyl groups, causing slight shifts in the methyl asymmetric and symmetric deformation vibrations.

For TMPA-montmorillonites, the wavenumber position of the methyl δ_a vibration of adsorbed TMPA ($\approx$1490 cm^{-1}) increased by about 2 cm^{-1} as P/P_0 increased from 0 to about 0.20, corresponding to about

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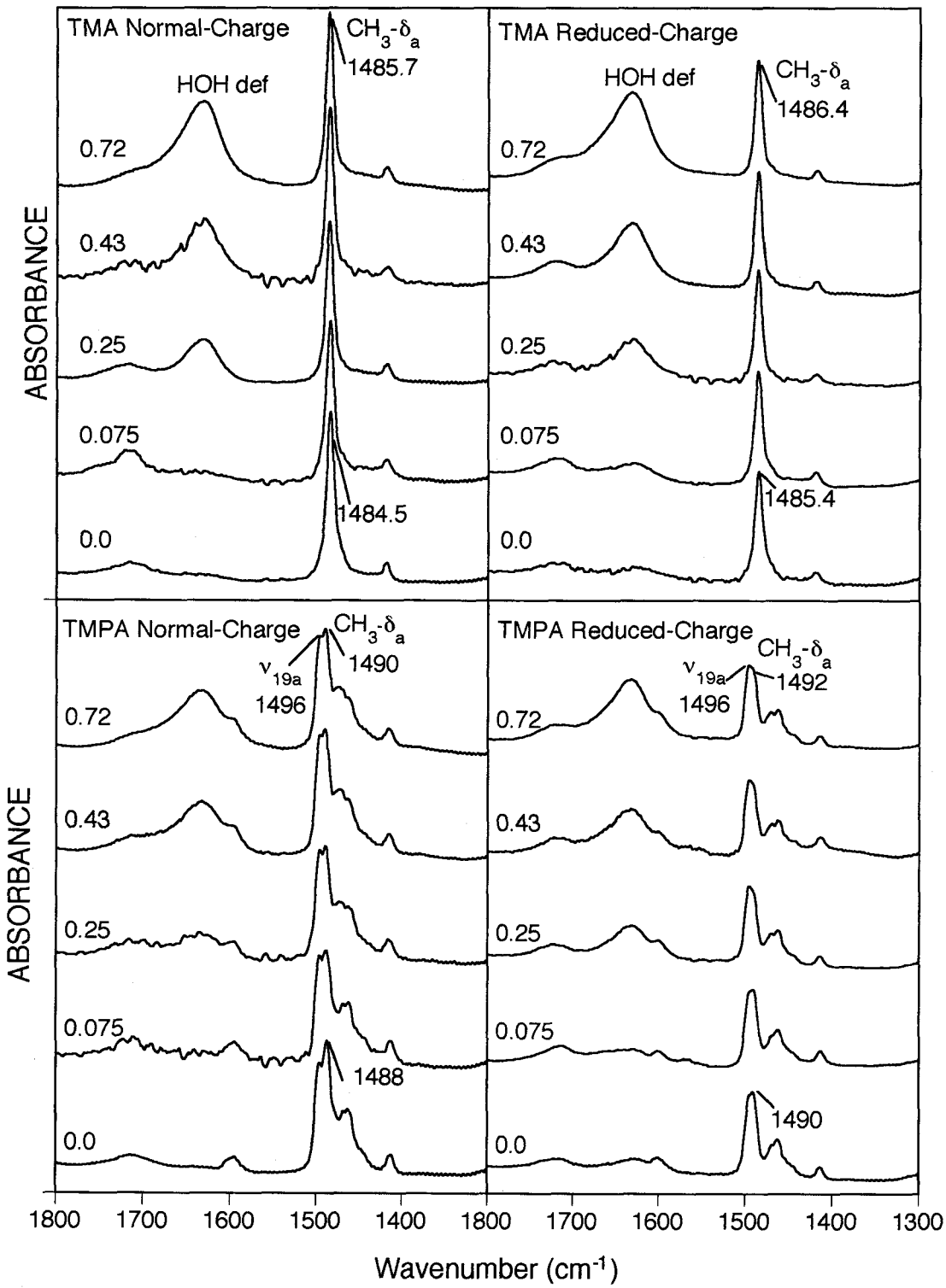


Figure 4. Infrared spectra of normal-charge and reduced-charge TMA- and TMPA-montmorillonites at selected partial water pressures.

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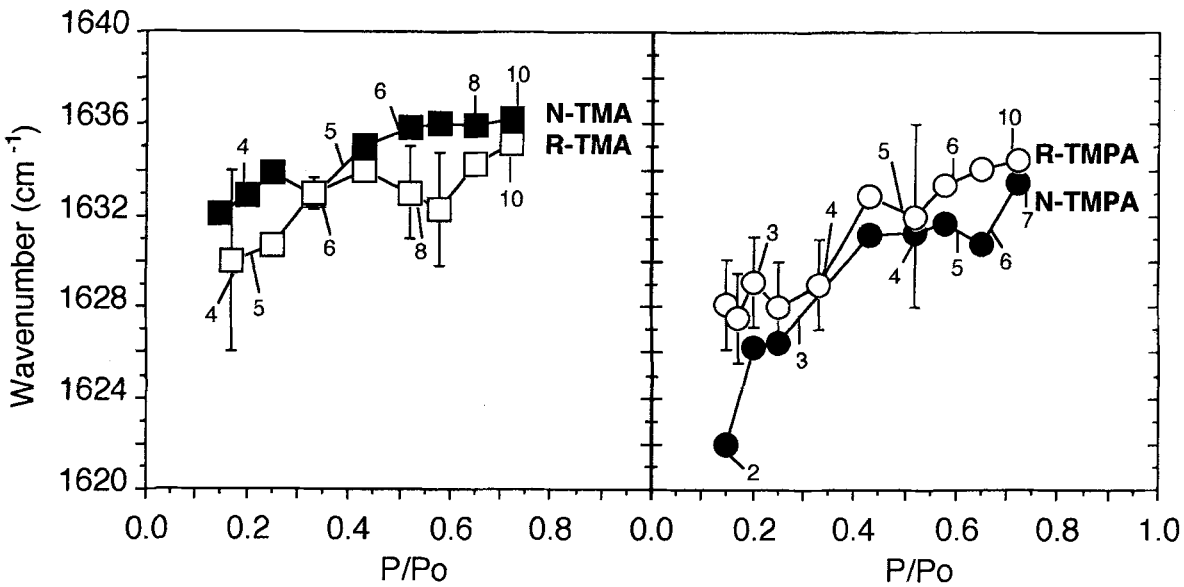


Figure 5. Effect of partial water vapor pressure (P/P_0) on wavenumber position of HOH deformation band of water adsorbed on normal-charge (N) and reduced-charge (R) TMA- and TMPA-montmorillonites. Numerals in figure indicate number of water molecules per cation at given P/P_0.

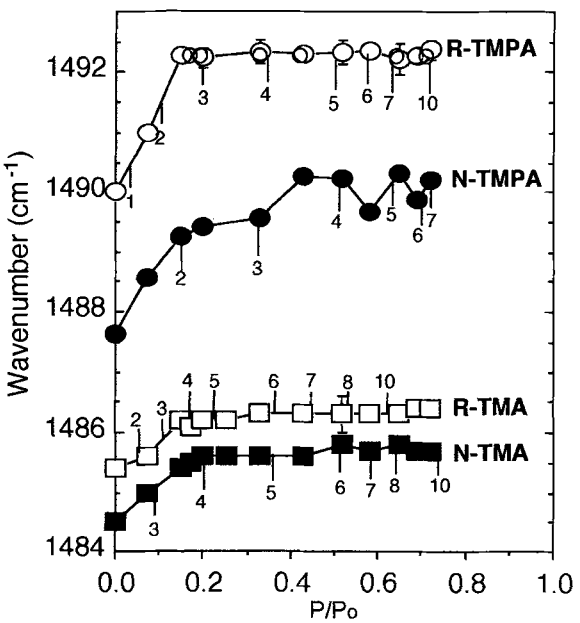


Figure 6. Effect of partial water vapor pressure (P/P_0) on wavenumber position of methyl asymmetric deformation vibrations of TMA and TMPA adsorbed on normal-charge (N) and reduced-charge (R) Wyoming montmorillonites. Numerals in figure indicate number of water molecules per cation at given P/P_0.

2.5 water molecules per cation for both charge treatments (Figure 6b). The methyl symmetric vibration exhibited a similar trend, although this vibration is weakly absorbing and there was more scatter in the position of the symmetric deformation peak (data not shown). The position of TMPA's C-H out-of-plane deformation vibration, which should be sensitive to interactions between water and the phenyl ring, was unaffected by water sorption, as were the ν_{19a} and ν_{19b} ring stretching vibrations (data not shown). These results, together with the HOH deformation results, support the contention that the affinity of water for TMPA ions is greater than the affinity of water for the siloxane surface, even though TMPA is relatively insoluble in water and has a low hydration energy. The fact that the methyl deformation vibrations, but not the ring vibrations, shift as the first few H_2O molecules are adsorbed indicates that water interacts preferentially with the methyl portion of TMPA, not with the aromatic ring.

CONCLUSIONS

The macroscopic and spectroscopic results reported in this paper show that TMA and TMPA are more hydrophilic than is the siloxane surface. Normal-charge and reduced-charge TMA-montmorillonites adsorbed more water at a given P/P_0 than did their TMPA-saturated counterparts, as would be expected if adsorbed water hydrates the organic cation, not the siloxane surface. In addition, water sorption was greater for normal-charge montmorillonites, which have more adsorbed cations, than for reduced-charge montmorillonites, which have greater N_2-accessible (and H_2O-accessible) surface areas. Infrared spectroscopy provided molecular-level evidence that water interacts with adsorbed TMA and TMPA even though these or-

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ganic cations are only very weakly hydrated. The wavenumber positions of the HOH deformation vibration of adsorbed water and of the methyl asymmetric vibrations of adsorbed TMA and TMPA increased as the amount of adsorbed water increased. These results should aid our understanding of the mechanism by which water inhibits sorption of nonionic organic compounds on TMA- and TMPA-montmorillonites.

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