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

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