FTIR Study of Competitive Water-Arene Sorption on Tetramethylammonium- and Trimethylphenylammonium-Montmorillonites

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Abstract: Montmorillonites saturated with small quaternary alkylammonium ions such as tetramethylammonium (TMA) or trimethylphenylammonium (TMPA) are excellent sorbents for aromatic pollutants. In some cases, water inhibits arene sorption, but the inhibition mechanism is not understood completely. The objectives of this study were to determine whether arenes interact with adsorbed TMA and TMPA ions and/or with siloxane surfaces, and how water affects these interactions. We reacted benzene and ethylbenzene vapors with normal- and reduced-charge TMA- and TMPA-montmorillonite films at several relative humidities, and obtained infrared spectra of the resulting sorbate-clay complexes. Arene sorption caused the methyl asymmetric deformation vibrations adsorbed TMA and TMPA to shift to lower wavenumber, whereas water sorption caused shifts to higher wavenumber. In the absence of water, benzene and ethylbenzene adsorbed on the siloxane surface as well as interacted directly with TMA and TMPA ions. The proportion of TMA and TMPA ions that interacted with benzene and ethylbenzene was greater for reduced-charge than normal-charge montmorillonite. Comparison of the HOH deformation and cation methyl asymmetric deformation vibrations indicated that both benzene and ethylbenzene inhibited water sorption substantially, and that water more readily displaced benzene and ethylbenzene from TMA and TMPA ions than from siloxane surfaces. Water inhibited arene sorption mainly by hydrating exchangeable cations, thereby obscuring siloxane surfaces adjacent to adsorbed TMA and TMPA ions and decreasing the average pore dimensions. These results indicate that in the presence of bulk water, arene adsorption likely occurs primarily on the siloxane surface.

Key Words: Alkylammonium • Benzene • Ethylbenzene • Infrared spectroscopy • Organoclay • Sorption • Water

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