

Crystalline Swelling of Organo-Modified Clays in Ethanol – Water Solutions

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Abstract:

The swelling of organo-modified clays in organic solvents may have important consequences on bulk properties of materials based on this technology. X-ray powder diffraction was used to study the swelling of orientated films of dioctahedral smectites exchanged with benzyloctadecyldimethylammonium (BODMA) equilibrated in ethanol-water solutions. The influence of total layer charge and the location of the layer charge on swelling of two organo-modified bentonites and three organo-modified reference smectites in ethanol:water solutions were evaluated. The measured interlayer spaces of BODMA smectites equilibrated in water increased with total layer charge and with the relative amount of tetrahedral charge. At intermediate ethanol concentrations a distinct plateau was observed in the swelling profiles of BODMA smectites having layer charges $> 0.8 e^-$ per $O_{20}(OH)_4$. When equilibrated in ethanol, all BODMA smectites expanded to similar values (34-36 Å). The magnitude of the change in crystalline swelling of organo-smectites in ethanol compared to that in water was found to be inversely proportional to total layer charge density, but proportional to the ratio of octahedral to tetrahedral layer charge. Calculations using NEWMOD showed that the d-spacings measured were unlikely to be due to interstratifications of fully water-solvated with fully ethanol-solvated BODMA smectite layers. Introduction of up to 2.0 M aqueous NaCl resulted in a slight (~ 0.5 Å) decrease in the interlayer spacing of BODMA-montmorillonite. However, 0.02 and 0.2 M NaCl added to ethanol:water mixtures enhanced interlayer expansion in these miscible solvents. The results suggest that inorganic salt depressed the activity of water in ethanol:water mixtures, and thereby increased the proportion of ethanol actually penetrating the interlayer spaces of BODMA smectites. A plausible mechanism is discussed to describe the observed interlayer expansion in ethanol:water solutions and how this might impact possible applications.

key words: *swelling; organo-clays; bimolecular layers; permeable reactive barriers; quaternary ammonium cations; water activity*