
Crystalline Swelling of Smectite Samples in Concentrated NaCl Solutions in Relation to Layer Charge

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Abstract: The basal spacing of a set of smectites, with layer charges between 0.74 and 1.14 electrons per unit cell, have been measured while the smectites were in equilibrium with NaCl solutions having concentrations of 0.25 to 2.5 molal. Except for the most highly charged smectites, an expansion from ~ 15.5 to ~ 18.5 Å occurred as the NaCl concentrations were reduced. This expansion (or "crystalline swelling") corresponds to the transition from two to three sheets of water between the silicate layers. A random interstratification of 15.5 and 18.5 Å structure units was present during the change and gave rise to broad diffraction peaks for the 001 reflections. A balance between cation hydration forces, interlamellar electrostatic forces, and van der Waals forces was apparently the basis of the relationship between surface charge and swelling. The results can be expressed in terms of the relative vapor pressures at which the transitions were half complete; these pressures increased with surface density of charge, and over the range of surface charge studied, the P/P_0 values ranged from 0.943 to 0.974.

Key Words: Electrolyte • Layer charge • Smectite • Swelling • Vapor pressure • X-ray powder diffraction

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