
Infrared Study of Water Sorption on Na-, Li-, Ca-, and Mg-Exchanged (SWy-1 and SAz-1) Montmorillonite

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Abstract: An environmental infrared microbalance (EIRM) cell was used to study H₂O sorption on two montmorillonite samples as a function of water content and type of exchangeable cation. The vibrational spectra showed that H₂O sorbed to the clay at low-water content was strongly influenced by the exchangeable cation and by the close proximity to the clay surface. At water contents <6 H₂O molecules per exchangeable cation, the H-O-H bending mode of H₂O (ν_2 mode) shifts to a lower frequency and is characterized by an increase in molar absorptivity. In contrast, the positions of the asymmetric and symmetric OH-stretching modes of sorbed water (ν_1 and ν_3 modes) shift to higher energies. These observations indicate that H₂O molecules sorbed to the clay surface at low-water content are less hydrogen bonded than in bulk H₂O. In addition, the vibrational-stretching and bending bands of the structural OH groups of the 2:1 layer are also strongly influenced by H₂O content and type of exchangeable cation. By using the EIRM cell, the molar absorptivities of the structural OH-bending vibrations were measured as a function of H₂O content. The position and molar absorptivity of the structural OH-bending bands at 920, 883, and 840 cm⁻¹ are strongly influenced by H₂O content and type of exchangeable cation. The molar absorptivity of the 920-cm⁻¹ band, which is assigned to the AlAlOH group, decreased strongly at low-H₂O content. This reduction in intensity is assigned to a dehydration-induced change in orientation of the structural OH groups resulting from the penetration of H₂O molecules into siloxane ditrigonal cavities that are not associated with a net negative charge from isomorphous substitutions.

Key Words: Exchangeable Cation • FTIR • Hydration • Hysteresis • Smectite • Sorption • Water

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