



Confined H₂O in Micro/Mesoporous Silicates: Bonding, Vibrational and Thermodynamic Behavior

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Many micro/mesoporous silicates are hydrophilic. However, a physicochemical description for their mineral-H₂O-molecule interactions is not at hand. We are studying the behavior of confined H₂O in various micro/nanoporous silicates to better understand the nature of the local interactions and the macroscopic thermodynamic properties. Calorimetric heat capacity (C_p) and DTA/TG determinations and powder IR and polarized single-crystal Raman spectroscopy are being used to investigate thermodynamic, bonding and vibrational behavior.

The first group of studied microporous silicates, namely cordierite, Mg₂Al₄Si₅O₁₈xH₂O and beryl, Be₂Al₃Si₆O₁₈xH₂O, can hold single H₂O molecules in small microcavities. The molecules can exchange with the environment with no change in molar volume of either phase. The C_p behavior of the confined H₂O, which interacts via weak van-der-Waals forces to the aluminosilicate framework, is greater than that for ice at $T < 100$ K, but roughly similar to that of steam at $T > 100$ K. Raman, IR and inelastic neutron scattering measurements show that the H₂O molecule is quasi free in both phases. In cordierite, external translational, T(H₂O), modes occur at 80 and 48 cm⁻¹ and a librational mode, L(H₂O), at 218 cm⁻¹, as based on inelastic neutron scattering spectroscopy (Winkler and Hennion, 1994). For beryl, Raman spectra indicate an external T(H₂O) mode at about 10 cm⁻¹ and L(H₂O) modes at 190 and 205 cm⁻¹.

Micro/mesoporous zeolites (e.g., natrolite-Na₁₆[Al₁₆Si₂₄O₈₀]·16H₂O, scolecite-Ca₈[Al₁₆Si₂₄O₈₀]·24H₂O, and gmelinite-(Na₂,Ca)[Al₂Si₄O₁₂]·6H₂O) constitute a

second, large group of hydrophilic silicates. Here, the H₂O molecule shows various degrees of hydrogen bonding with different C_p behavior. In general, zeolites show, unlike beryl and cordierite, measurable changes in their volumes with loss or gain of H₂O. In small-pore zeolites, such as parnatrolite, C_p behavior for H₂O behaves roughly similar to that for ice at T < 100 K. At T > 100 K, C_p increases and is greater than the C_p of ice and also for H₂O in cordierite at T > 250 K. In natrolite and scolecite, T(H₂O) modes occur between 45 and 180 cm⁻¹ and L(H₂O) modes at roughly 430-440 cm⁻¹. In the case of gmelinite, which is characterized by large as well as small pores, the total C_p behavior is “normal” at 0 K < T < 200 K. However, it then increases anomalously at T > 200 K as compared the C_p behavior for many zeolites. The vibrational properties for the H₂O molecules are not known, but the large increase in C_p could be due to a weakening in H-bonding.

Several conclusions are: 1) At T < 200 K, C_p behavior of confined H₂O in micro/mesoporous silicates is controlled by the nature of low-energy external L(H₂O) and T(H₂O) modes. 2) The energies of L/T(H₂O) modes reflect weak van-der-Waals and weak to moderately strong hydrogen-bond forces. The nature of H-bonding plays a central role in affecting confined H₂O behavior in hydrophilic micro/mesoporous silicates. 3) The marked increase in C_p in some zeolites with increasing T may indicate a change in hydrogen bonding behavior from more “ice-like” to increasing “liquid-water-like”. 4) Macroscopic C_p and entropy values for confined H₂O in silicates cannot be considered similar, as is done in crystal-chemical-based schemes that are used for modeling thermodynamic properties of H₂O-bearing silicates.