A Raman and X-ray absorption spectroscopic investigation of the structure and speciation of aqueous zinc bromide solutions at hydrothermal conditions

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A Raman spectral study was carried out on three aqueous solutions of varying concentration and bromide/zinc ratio. Spectra were collected at 11 different temperature-pressure conditions ranging from ambient to 500°C and up to 0.9 GPa. Raman band assignments for aqueous zinc bromide complex species reported in previous studies were used to determine the relative concentrations of $ZnBr_4^{2-}$, $ZnBr_3^-$, $ZnBr_2$, and $ZnBr^+$ species at various temperatures and pressures. Our results are in close agreement with X-ray absorption spectroscopic (XAS) data, and confirm that the tetrabromo zinc complex, $ZnBr_4^{2-}$, is the predominant species up to 500°C in solutions having high zinc concentrations (1 *m*) and high bromide/zinc molar ratios ([Br]/[Zn] = 8). This result is consistent with the observed predominance of the $ZnCl_4^{2-}$, complex in chloride-rich fluid inclusion brines at high temperatures. In agreement with previous solubility and Raman spectroscopic experiments, our measurements also indicate that species with a lower number of halide ligands and charge are favored with increasing temperature in dilute solutions, and solutions with low bromine/zinc ratios ([Br]/[Zn] < 2.5). Raman and X-ray absorption spectroscopy are complementary techniques that were used in this study to obtain speciation and structural data on aqueous zinc bromide solutions at elevated temperatures and pressures. Furthermore, we show that Raman spectroscopy, in some cases, may be used to independently evaluate XAS data obtained from high temperature disordered systems such as supercritical fluids.

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