

X-ray absorption spectroscopic studies of halide ion hydration in hydrothermal solutions

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Ion-solvent interaction comprises the fundamental aspect of aqueous solution chemistry and is defined to a considerable extent by the properties of water solvent at any given temperature and pressure. We are currently studying ion hydration, ion pairing and metal complex equilibria in hydrothermal solutions at temperatures up to 450°C and 2000 bar using X-ray absorption spectroscopy. The X-ray optical cell employs various types of windows which may be CVD or single crystal diamond, glassy carbon or silica.

Our on-going studies on ion hydration indicate that for many cations, the first shell cation-oxygen(water) distances contract with increasing temperature as the hydrogen bonded network of the bulk solvent becomes disrupted [1]. The observations for the simple halide anions is quite different. In the case of the iodide ion for example, the iodide-oxygen(water) distance expands from 3.56 to 3.63 Å and the anion “dehydrates” as the number of first shell waters decreases from 7 to 4 as temperature increases from ambient to 350°C at the equilibrium saturated vapour pressure. These observations are supported by our ab initio/molecular dynamics simulations and high temperature uv spectroscopic data. At the same time, pulsed electron high pressure mass spectrometric studies [2] on halide ion water clusters suggest that surface cluster hydrated ions may predominate in less dense hydrothermal fluids.

References

- [1] Seward T.M. and Driesner T. (2004) In: Steam, Water and Hydrothermal Solutions: The Physical Chemistry of Aqueous Systems at Elevated Temperatures and Pressures, (eds. D.A. Palmer, R. Fernandez-Prini and A.H. Harvey), Elsevier, chap. 5, 149-182.
- [2] Likholyot A., Hovey J.K. and Seward T.M. (2005) Geochim. Cosmochim. Acta 69, 2949-2958.