

X-ray Absorption Spectroscopic (EXAFS) measurements on aqueous solutions to 350°C

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With increasing temperature to the critical point, the decrease in hydrogen bonding in liquid water (Chialvo and Cummings, 1996) gives rise to fundamental changes in ion-solvent interaction (Driesner *et al.*, 1998). These effects are manifested by changes in ion-oxygen water bond lengths with associated decreases in ion-water coordination numbers with increasing temperature (Seward *et al.*, 1996; 1998; Fulton *et al.*, 1996; 1997). Information on such changes is important to the understanding of many aspects of hydrothermal solution chemistry such as, for example, the fractionation of oxygen and hydrogen isotopes in high temperature aqueous systems in the earth's crust (Driesner and Seward, 1998). We report here some of our recent measurements of ion-oxygen (water) distances in high temperature aqueous electrolyte solutions using EXAFS.

Experimental methods

The X-ray absorption spectra were collected at the CCLRC Daresbury synchrotron light source (2 GeV) with an average beam current of 150 mA. The measurements were carried out on a beam line having Wiggler enhanced brightness. Most of the spectra were collected in fluorescence mode using a 13-element Canberra detector. The solutions were contained in a high temperature cell employing

silica glass windows. Another cell has also been constructed which contains diamond windows and is designed to operate up to 500°C and 2000 bars pressure. The background corrected spectra were analysed in k-space using the EXCURV92 program (Binstead *et al.*, 1991). This facilitates phase shift corrections using Hedin-Lundquist potentials. The statistical significance of each shell was evaluated using the method of Joyner *et al.* (1987).

Results and discussion

Data on ion-oxygen (water) bond lengths obtained from EXAFS are given in Table 1 and were chosen to demonstrate some of the changes associated with aquations of different charge and size. It is interesting to note that the cation hydration shell contraction is greatest (i.e. 0.10 Å) for the soft, univalent silver ion and less (i.e. 0.05 Å) for the divalent Sr²⁺ and Cd²⁺. The In³⁺-oxygen (water) distance shows no change over the temperature investigated. On the other hand, the iodide-oxygen (water) distance remains little changed up to ~200°C and then exhibits a small expansion of the solvation shell. In all cases for both cations and anions, the ion-oxygen (water) distances are also associated with a decrease in the number of coordinated water molecules. This latter observation is consistent with the temperature induced red shift of charge-transfer-to-solvent spectra in the ultraviolet

TABLE 1. Ion-oxygen (water) distances (Å) as a function of temperature at saturated vapour pressure

<i>t</i> /°C	Ag ⁺	Sr ²⁺	Cd ²⁺	In ³⁺	I
25	2.32	2.57	2.27	2.13	3.55
100	2.30	2.55	2.25	2.13	3.56
200	2.27	2.53	2.24	2.13	3.56
300	2.22	2.52	2.22	—	3.61

region for the hydrated iodide ion. In addition, molecular dynamics simulations of chloride ion hydration (Driesner *et al.*, 1998) also show a small expansion of the chloride ion solvation shell. These solvation effects play an important role in the chemistry of many processes operating in the earth's crust.

References

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