

Synchrotron EXAFS study of hydrothermal AgNO_3 solutions

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Introduction

The understanding of many geochemical transport processes involving aqueous solutions at high temperatures and pressures is fundamentally premised on knowledge of aqueous electrolyte chemistry and metal complex equilibria under hydrothermal conditions. To date, there are few studies of metal cation solvation and coordination geometry in aqueous media under extremes of temperature and pressure. We report here the results of our on-going experiments to measure X-ray absorption spectra of aqueous solutions at elevated temperatures. Preliminary data on strontium, cadmium and indium - containing solutions will also be discussed.

Experimental methods

The high temperature EXAFS spectra were obtained using a purpose - built optical cell (silica windows) at the Daresbury synchrotron facility which operates at 2 GeV with an average current of 150mA. Silver K-edge (25.521 keV) EXAFS data were collected in both transmission and fluorescence modes using a beam line with Wiggler enhanced brightness. The data were analysed using the program EXCURV90 (Binsted *et al*, 1990) which makes use of single scattering curved wave theory for calculation of the EXAFS (Gurman *et al*, 1984). Theoretical fits were generated by defining shells of backscatters and then integrating the distances, R , and the Debye - Waller factors, $2\sigma^2$, to give the best agreement with the experimentally derived spectra.

Results

Figure 1 gives the EXAFS spectrum and its Fourier transform for a 0.10M AgNO_3 solution at 25°C. Figure 2 gives the Fourier transforms of the EXAFS with varying temperature from 25 to 300°C. The spectra show little or no decrease in the amplitude of the EXAFS and no significant

change occurred in refined Debye - Waller factors (table 1). Our data confirm that Ag^+ is tetrahedrally coordinated in AgNO_3 solutions because similar bond lengths ($\sim 2.3 \text{ \AA}$) have been reported in crystalline solids in which Ag^+ is in four - fold, tetrahedral coordination. The first shell silver - oxygen distances decrease from 2.30 to 2.26 \AA over a temperature range from 25 to 300°C.

We have fitted the second shell at 3.15 \AA at 25°C with a single nitrogen atom and there is some indication that two nitrogens are present in the

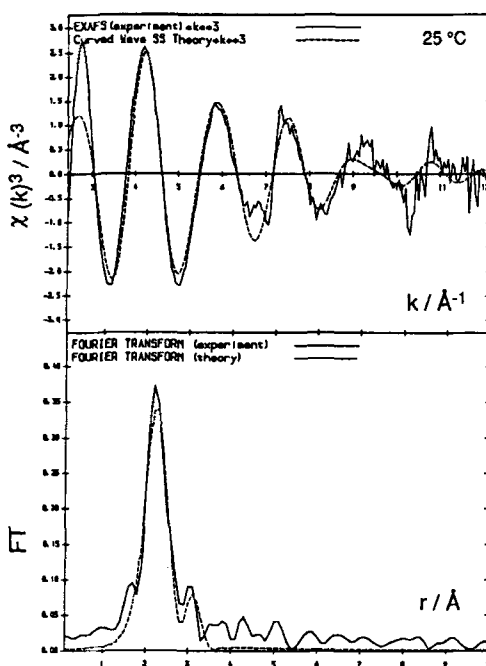


FIG. 1. k^3 weighted EXAFS background subtracted spectrum and its Fourier transform for 0.10 M AgNO_3 at 25°C.

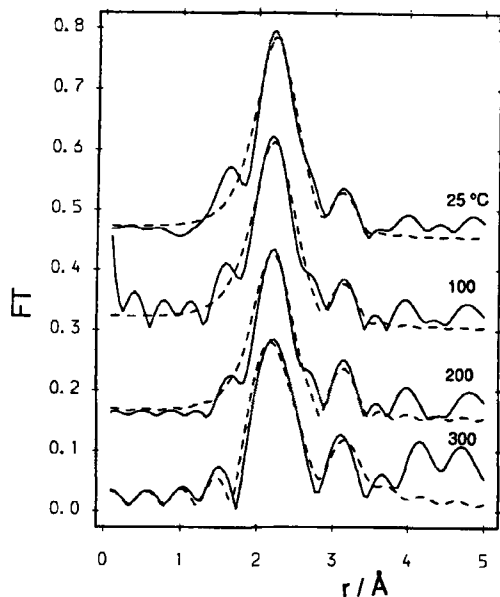


FIG. 2. Fourier transforms of the EXAFS for 0.10m AgNO_3 from 25 to 300°C.

second shell at 300°C. These data indicate that AgNO_3 ion pairs exist in aqueous solutions and that the formation of these ion pairs is enhanced by increasing temperature. Ag^+ has a low affinity for oxygen donors and accordingly, water dipoles are only weakly bound to $\text{Ag}^+(\text{aq})$. The apparent decrease in the average silver oxygen distance (Table 1) probably arises from increased formation of silver - nitrate ion pairs. The attractive

TABLE 1. Preliminary X-ray absorption data for 0.10m AgNO_3 solutions

t/°C	scatterer	N (a)	R/Å (b)	$2\sigma^2/\text{Å}^2$ (c)
25	O	1	2.30	0.030
	N	1	3.15	0.015
100	O	4	2.28	0.034
	N	1	3.16	0.013
200	O	4	2.27	0.038
	N	1	3.16	0.014
300	O	4	2.26	0.030
	N	1	3.15	0.005

(a) number of backscatterers in shell (b) distance of central atom (Ag) to backscatterers (c) Debye - Waller Factor.

force between Ag^+ and embed Equation will be greater than that between Ag^+ and H_2O molecules, thus leading to a small, average, silver - oxygen bond contraction.

References

- Binsted, N., Campbell J.W., Gurmann S.J. and Stephenson P.C. (1990) SERC Daresbury Laboratory EXCURV90 Program.
 Gurman S.J., Binsted N. and Ross I. (1984) *J. Phys. C*, 17, 143-51.