J. Synchrotron Rad. (1999). **6**, 607–608

High-temperature indium(III) solutions

John M. Charnock[a,b*], **C. Michael B. Henderson**[a,b] **and Terry M. Seward**[c]

[a]*Department of Earth Sciences, The University of Manchester, Oxford Road, Manchester M13 9PL, U.K.*
[b]*CLRC Daresbury Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, U.K.*
[c]*Institut für Mineralogie und Petrographie, ETH-Zentrum, CH-8092 Zürich, Switzerland*

The speciation of metal ions in high-temperature, high-pressure aqueous solutions is important in geochemical and environmental processes, such as metal transport and ore formation. Changes in the fundamental properties of water with temperature will affect the number and type of ligands around the metal and the degree of ion pair formation. X-ray absorption spectroscopy allows these changes to be monitored. We have investigated the solvation and stepwise complex formation of In(III) in aqueous solutions up to 350 C. In solutions containing perchlorate and nitrate ions there was no change in the In-O bond length (2.13 Å), and no ion pairing with nitrate ions. In chloride solutions both O and Cl are present in the inner coordination sphere, with the proportion of Cl increasing with increasing temperature and Cl molality.

Keywords: EXAFS, indium, solution

1. Introduction

A knowledge of the physical geochemistry of high-temperature, high-pressure aqueous media is crucial in understanding metal complexation in systems of geochemical and environmental importance. Increasing temperature leads to major changes in the fundamental properties of water, such as, for example, the dielectric constant which decreases dramatically from 80.3 at 20 C to 8.7 at 370 C at equilibrium saturated vapour pressures. These changes result in significant changes in the coordination behaviour of metal ions at elevated temperatures. The few existing studies indicate that with increasing temperature there is a tendency towards the formation of neutral species or species of low charge. Thus, a 0.1 molal solution of a simple 1:1 salt such as sodium chloride, which is completely dissociated into hydrated ions at room temperature, is about 50% associated into Na^+Cl^- ion pairs at 300 C. In addition there is often a change in coordination geometry with increasing temperature, for example from octahedral to tetrahedral. These changes have not been well studied and have been inferred from changes in the entropies of stepwise complex formation and from a handful of visible and Raman spectroscopic studies of high temperature solutions.

In previous work using X-ray absorption spectroscopy to analyse aqueous solutions containing univalent Ag^+ (Seward et al. 1996) and divalent Sr^{2+} (Seward et al. 1998) ions we have shown that on increasing the temperature from 25 C to 350 C the metal-oxygen (water) distances decrease in both nitrate and perchlorate solutions over a range of concentrations. These changes result from two mechanisms: (i) a decrease in the average number of water molecules in the solvation shell around the metal ion, and (ii) a dynamic effect which shortens the mean residence time of the water molecules in the solvation shell. In strontium solutions containing chloride ions there was also an increase with increasing temperature in the number of chlorides coordinated to each strontium, and at the highest temperatures there was clear evidence for some degree of clustering and the formation of multinuclear species. Other groups have obtained similar results with, for example, zinc chloride (Anderson et al. 1998) and nickel bromide (Wallen et al. 1998).

We have extended our work to study the behaviour of the trivalent metal cation In^{3+}, in solutions containing nitrate, perchlorate, and chloride anions, and at temperatures up to 350 C. This may be expected to show differences in its behaviour from that shown by uni- and divalent cations because: (i) the exchange lifetimes of water ligands in the hydration sphere are longer, and (ii) In^{3+} is extensively hydrolysed in near neutral aqueous media.

2. Experimental

The solutions were sealed in half-filled silica tubes (i.d. 4-6 mm, o.d. 6-8 mm), allowing room for the solution to expand on heating. The tubes were mounted in an aluminium heating block with windows cut out to allow either transmission or fluorescence measurements. The temperature was controlled using electrical heating elements, and monitored with thermocouples (see Seward et al, 1996 for details).

The XAS data were collected at in transmission (conc. 0.1m) or fluorescence (0.01m) modes on station 9.2 of the CLRC Daresbury Synchrotron Radiation Source, operating at 2 GeV with an average current of 150 mA. A Si(220) double crystal monochromator was used, detuned to reject 50% of the incident signal in order to minimise harmonic contamination. Io and It were measured using ion chambers filled with a mixture of Kr/He, and the fluorescence signal was collected using a solid state 13-element Canberra detector windowed on the In Kα fluorescence signal. Two-four scans were collected and summed at each temperature for the transmission data. Four-sixteen scans were collected for each fluorescence spectrum.

The isolated EXAFS spectra were analysed using EXCURV97 (Binsted et al., 1997), employing the spherical wave approximation (Lee & Pendry, 1977; Gurman et al., 1984). Phaseshifts were derived from ab initio calculations using Hedin-Lundqvist potentials and von Barth ground states (Hedin & Lundqvist, 1969). The theoretical fits were obtained by adding shells of backscattering atoms around the central absorber atom and refining the Fermi energy, Ef, the absorber-scatterer distances, r, the numbers of scatterers, N, and the Debye-Waller factors, $2\sigma^2$, in order to minimise the sum of the square of the residuals between the experiment and the theoretical fit (R-factor). The possibility of non-Gaussian pair distribution functions was tested using cumulant expansions, but in no case did this significantly improve the fit or change the fit parameters. Therefore a Gaussian distribution was used.

3. Results and Discussion

3.1 *Nitrate solutions*

The nitrate solutions showed no decrease in the metal-oxygen distance, and no clear decrease in coordination number, up to 250 C (Table 1). There was no evidence for ion pairing, even at the highest temperatures.

Table 1
EXAFS analyses of (a) 0.01m $In(NO_3)_3$ in 0.1m HNO_3 , and (b) 0.1m $In(NO_3)_3$ in 0.1m HNO_3 solutions.

T / C	Shell	r / Å	$2\sigma^2$ / Å^2	R-factor
30^a	6.3 x O	2.14	0.008	28.9
100^a	6.5 x O	2.13	0.010	43.7
200^a	5.4 x O	2.12	0.017	52.2
30^b	6.4 x O	2.13	0.008	13.4
100^b	6.5 x O	2.13	0.011	14.2
200^b	6.5 x O	2.13	0.014	14.9
250^b	6.3 x O	2.14	0.021	20.4

N is no. of scatterers± 20%, r is distance± 0.02Å. $2\sigma^2$ is the Debye-Waller factor ± 20%

3.2 *Perchlorate solutions*

In the 0.01m $In(ClO_4)_3$ in 0.01m $HClO_4$ solution the In-O distance and the coordination number remained constant between 30 C and 200 C. The solutions started to break down at higher temperatures. The 0.1m $In(ClO_4)_3$ in 1.0m $HClO_4$ solution also showed no change in coordination number or bond length up to 250 C (Table 2). However, even at 30 C there is clear evidence of ion pair formation, with a chlorine atom at 3.14Å consistent with at least one oxygen-bound perchlorate coordinated to the indium. Inclusion of this interaction in the fits significantly improves the R-factor (residual) at every temperature.

Table 2
EXAFS analyses of (a) 0.01m $In(ClO_4)_3$ in 0.01m $HClO_4$, and (b) 0.1m $In(ClO_4)_3$ in 1.0m $HClO_4$ solutions.

T / C	Shell	r / Å	$2\sigma^2$ / Å^2	R-factor
30^a	6.4 x O	2.14	0.010	38.5
100^a	6.3 x O	2.13	0.012	27.0
200^a	6.1 x O	2.13	0.012	29.5
30^b	6.4 x O	2.13	0.008	9.7
	1.0	3.14	0.033	
100^b	6.4 x O	2.13	0.010	12.5
	1.5	3.13	0.034	
200^b	6.3 x O	2.13	0.012	9.7
	1.8	3.14	0.045	
250^b	6.3 x O	2.13	0.013	14.0
	1.5	3.14	0.037	

N is no. of scatterers ± 20%, r is distance ± 0.02Å, $2\sigma^2$ is the Debye-Waller factor ± 20%

3.3 *Chloride solutions*

In the indium chloride solutions the inner coordination sphere comprises oxygens (water) and chlorides (Table 3). On heating the solutions the water is replaced by chloride around the indium. In all the solutions there is a decrease in the indium-chloride distance with increasing temperature, and an increase in the indium-oxygen distance is consistently observed in every solution. The decreasing In-Cl distance reflects a decrease in the total coordination number. The increase in the In-O distance may be related to the effect of the increasing numbers of negatively charged chlorides around the central cation reducing the effective charge density at the metal centre, in addition to the steric effect of the large chloride ions.

Table 3
EXAFS analyses of (a) 0.1m $InCl_3$ in 0.1m HCl , and (b) 0.1m $InCl_3$ in 1.0m HCl solutions.

T / C	Shell	r / Å	$2\sigma^2$ / Å^2	R-factor
30^a	4.3 x O	2.16	0.013	11.4
	2.6 x Cl	2.41	0.012	
100^a	4.0 x O	2.17	0.014	9.4
	2.6 x Cl	2.41	0.010	
200^a	3.1 x O	2.17	0.015	19.0
	2.9 x Cl	2.42	0.013	
300^a	2.5 x O	2.24	0.024	14.9
	3.8 x Cl	2.39	0.016	
350^a	2.1 x O	2.30	0.021	12.7
	4.5 x Cl	2.36	0.014	
30^b	2.8 x O	2.16	0.012	13.9
	3.9 x Cl	2.42	0.014	
100^b	2.5 x O	2.18	0.012	11.0
	3.9 x Cl	2.43	0.015	
200^b	1.9 x O	2.20	0.015	14.7
	3.7 x Cl	2.43	0.014	
300^b	1.4 x O	2.26	0.006	13.0
	3.9 x Cl	2.39	0.016	
333^b	1.3 x O	2.26	0.005	14.6
	3.8 x Cl	2.38	0.013	

N is no. of scatterers ± 20%, r is distance ± 0.02Å, $2\sigma^2$ is the Debye-Waller factor ± 20%

4. Conclusions

In the nitrate and perchlorate solutions the coordination sphere around the trivalent indium ion is less sensitive to increasing temperature than the corresponding anion solutions containing uni- and divalent ions. Ion pairing is observed in the perchlorate solution, but no evidence was seen for indium clustering. In the presence of chloride there is an increase in the In-O distance with increasing temperature, and a change to lower values for the average coordination number.

Acknowledgments

We are grateful to the CCLRC for provision of beamtime at the Daresbury SRS, and for all the assistance provided by Daresbury personnel, in particular Dr. Fred Mosselmans on station 9.2. The work was supported by the EPSRC, and additional funding provided by ETH-Zentrum, Zürich.

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(Received 10 August 1998; accepted 9 December 1998)