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Journal of Nuclear Materials 344 (2005) 100–103

journal of nuclear materials

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Structures of chloro-uranium species in molten LiCl–BeCl$_2$ eutectic: A combined X-ray and electronic absorption spectroscopy study

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Abstract

The structures and interatomic distances of various chloro complexes of uranium in LiCl–BeCl$_2$ eutectic melt at 380 °C have been determined from EXAFS measurements. Dissolution of UCl$_4$ and UO$_2$Cl$_2$ (in the absence of a chlorine atmosphere) generated UCl$_6^{2-}$ ions. Similarly, dissolution of UCl$_3$ generated UCl$_6^{3-}$ complexes but dissolution of UO$_2$Cl$_2$ under a chlorine atmosphere yielded a mixture of UCl$_6^{2-}$ and UO$_2$Cl$_4^{2-}$, deduced from electronic absorption spectra measurements. Interatomic distances and uranium coordination are compared with earlier data in molten LiCl, both in melts and for quenched samples at room temperature.

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1. Introduction

X-ray absorption spectroscopy is a direct element-specific technique providing information on the coordination state of elements in various media, including molten salts. Previously [1] we have studied LiCl-based melts containing uranium in all its principal oxidation states, +3, +4, +5 and +6. Beryllium chloride is similarly quite transparent to X-rays and also has a low melting point and forms a number of low-melting eutectics, thus allowing experiments to be conducted at lower temperatures. Be(II) is also a strong complexing agent and it was therefore of interest to investigate the behaviour of uranium in the presence of Be(II) ions in the melt. Care had to be taken with these melts due to the high toxicity of beryllium-containing vapours and dusts that potentially can arise from the relatively high vapour pressure prevailing at the temperatures involved.

2. Experimental

X-ray absorption spectra of molten and quenched samples were measured using the experimental set-up previously described [1]. These measurements were

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doi:10.1016/j.jnucmat.2005.04.024

performed on station 9.3 of the CLRC Daresbury Radiation Source, operating at a typical beam current of 150 mA and an energy of 2 GeV. The radiation was monochromated with a Si 220 double crystal. The spectra were summed, calibrated and the background subtracted using the Daresbury Laboratory programs EXCALIB and EXBACK. The spectra were simulated using EXCURV98 program.

The solvent used was the eutectic mixture of lithium and beryllium chlorides (m.p. 300 °C, containing 56 mol.% $BeCl_2$). Melts were prepared by fusing anhydrous salts mixed in the required proportions at 400–500 °C under dry argon, hydrogen chloride or chlorine atmospheres. To assist the dissolution of uranium compounds, the melt was also sparged with the appropriate gas. Uranium species were generated in the melt by adding anhydrous UCl_3, UCl_4 or UO_2Cl_2, prepared using standard methods. The composition and methods for preparing uranium-containing samples are listed in Table 1. To prevent the oxidation of U(III) when preparing U(III)-containing melts, a small piece of uranium metal was introduced into the cell. It was not however possible to obtain XAS data of acceptable quality from molten samples containing U(III) and subsequent analysis was therefore limited to that of the quenched samples.

Uranium concentrations in quenched melt samples were determined by ICP analysis and the average oxidation state by oxidimetry, as described previously [2]. The electronic absorption spectra of quenched melt samples were measured by diffuse reflectance (Fig. 1). All sample manipulations were performed in an argon-filled dry box. Specially designed sealed silica cells [1] were used for XAS measurements. The X-ray absorption spectra were recorded up to $k_{max} = 15$ Å^{-1} (maximum energy 18 keV) but the analysis of spectra was limited to

Table 1
Concentration and oxidation state of uranium in LiCl–$BeCl_2$ melts

Starting material and atmosphere	U (wt%)	U oxidation state
UO_2Cl_2 under Cl_2	7.30	4.23 ± 0.02
UO_2Cl_2 under HCl	7.71	3.87 ± 0.07
UCl_4 under HCl	5.75	3.76 ± 0.03
UCl_3 under Ar	11.66	3.01 ± 0.02

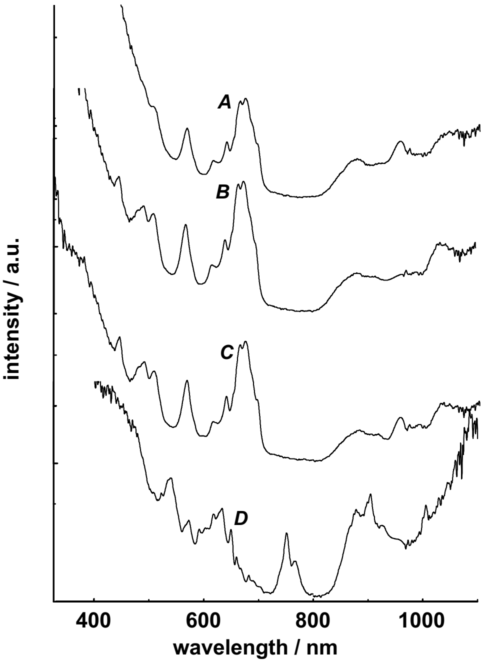

Fig. 1. Diffuse reflectance spectra of quenched LiCl–$BeCl_2$ melts containing uranium. Solutions initially obtained by dissolving UO_2Cl_2 under Cl_2 (A); UO_2Cl_2 under HCl (B); UCl_4 under HCl (C); and UCl_3 (D) under argon.

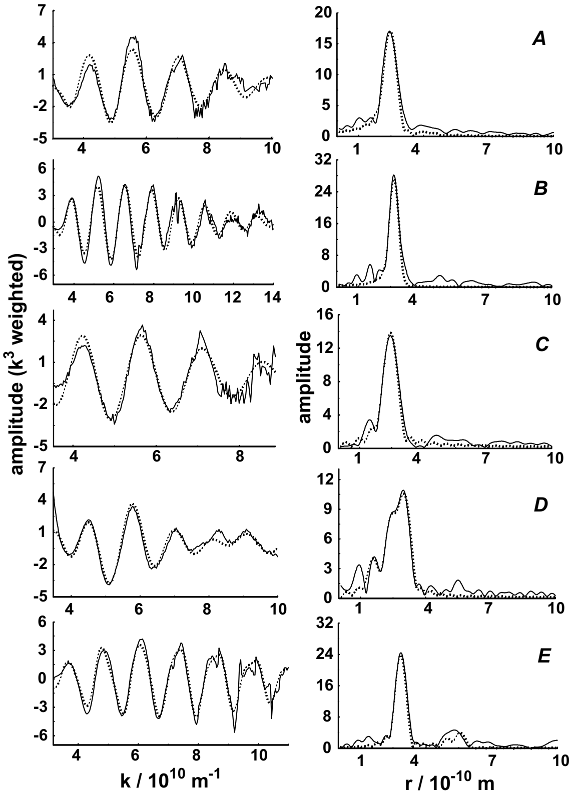

Fig. 2. Uranium L_{III}-edge EXAFS spectra in LiCl–$BeCl_2$ melts and corresponding Fourier transforms. Solution of UCl_4 at 380 °C (A); quenched sample at room temperature (B); solution of UO_2Cl_2 at 380 °C under Cl_2 (C); quenched sample at room temperature (D) and UCl_3 in quenched melt (E). Solid lines, experimental data; dashed lines, best fit.

k_{max} = 9–13 Å^{-1} due to the increasing ratio of noise-to-useful signal at higher energies. From the analysis of these truncated spectra the details concerning the nearest coordination environment of uranium in the various oxidation states could better be obtained.

3. Results and discussion

Uranium forms predominantly the chloro complexes of U(IV) and U(III) in LiCl–BeCl$_2$ melts (Table 1 and Fig. 1). After dissolving UCl$_4$ and UCl$_3$ in LiCl–BeCl$_2$ eutectic most of the uranium remained in the original oxidation state. Dissolution of UO$_2$Cl$_2$ under HCl atmosphere resulted in the reduction of uranium to the tetravalent state, and only in the presence of chlorine in the atmosphere was the mean oxidation state of uranium in the melt above four. In this latter case the system may, in principle, contain U(V) as well as U(VI) ions. The electron absorption spectra of U(V) complex ions in chloride melts contain broad overlapping bands at 620 and 800 nm [3–6] and these also remain in the spectra of the quenched melts [1]. Fig. 1 shows no band around 800 nm in the spectrum of the quenched melt, (obtained by dissolving UO$_2$Cl$_2$ in LiCl–BeCl$_2$ eutectic under Cl$_2$ atmosphere), indicating only U(IV) and U(VI) are present. Chemical analysis indicated the U(VI) content as 11–12%. Uranyl chloride is thermodynamically stable up to around 600 °C: however, in the presence of beryllium chloride, the following reaction can take place:

$$\mathrm{UO_2Cl_4^{2-} + 2BeCl_4^{2-} \rightarrow UCl_6^{2-} + 2BeO + Cl_2 + 4Cl^-} \qquad (1)$$

with the equilibrium strongly shifted to the right. Increasing partial pressure of chlorine in the atmosphere above the melt obviously shifts the equilibrium to the left stabilizing UO$_2$Cl$_4^{2-}$ complexes in the melt. Our previous studies [1] in pure LiCl melt at 750 °C showed that U(VI) is stable under Cl$_2$ atmosphere and forms UO$_2$Cl$_4^{2-}$ ions. This provides an additional evidence that the presence of Be(II) in the melt prevents the stabilization of uranyl ions, according to reaction (1).

Typical examples of uranium XAS (EXAFS and their corresponding Fourier-transforms) are shown in Fig. 2 and their analysis is given in Table 2. Hexachloro-coordinated ions UCl$_6^{n-}$ (n = 2 or 3) are present in U(III)- and U(IV)-containing melts, respectively, and the same ions and oxidation states are preserved in the quenched melt samples. It is also interesting to note that according to EXAFS spectroscopy dissolution

Table 2
Structural parameters from EXAFS curve fitting of uranium complexes in LiCl–BeCl$_2$ and LiCl melts

Melt system and fitting limit used	Shell U–X and co-ord no.	U–X (Å)	Debye–Waller factor (2σ^2) (Å)	*R*
UO$_2$Cl$_2$ in LiCl–BeCl$_2$ (atm. Cl$_2$), 380 °C, k_{max} = 9 Å^{-1}	U–O, 0.5	1.72	0.062	27.59
	U–Cl, 6	2.56	0.034	
UO$_2$Cl$_2$ in LiCl–BeCl$_2$ (atm. Cl$_2$), quenched melt, k_{max} = 13 Å^{-1}	U–O, 0.5	1.74	0.021	25.41
	U–Cl, 2	2.54	0.012	
	U–Cl, 4	2.74	0.019	
	U–U, 2	4.48	0.020	
UO$_2$Cl$_2$ in LiCl (atm. Cl$_2$), 750 °C, k_{max} = 10 Å^{-1}	U–O, 2	1.75	0.014	40.43
	U–Cl, 4	2.63	0.037	
UO$_2$Cl$_2$ in LiCl (atm. Cl$_2$), quenched melt, k_{max} = 13 Å^{-1}	U–O, 2	1.77	0.010	41.43
	U–Cl, 4	2.75	0.027	
UO$_2$Cl$_2$ in LiCl–BeCl$_2$ (atm. HCl), 380 °C, k_{max} = 9 Å^{-1}	U–Cl, 6	2.59	0.026	38.08
UO$_2$Cl$_2$ in LiCl–BeCl$_2$ (atm. HCl), quenched melt, k_{max} = 11 Å^{-1}	U–Cl, 6	2.71	0.024	26.63
UCl$_4$ in LiCl–BeCl$_2$ (atm. HCl), 380 °C, k_{max} = 10 Å^{-1}	U–Cl, 6	2.58	0.029	35.93
UCl$_4$ in LiCl–BeCl$_2$ (atm. HCl), quenched melt, k_{max} = 15 Å^{-1}	U–Cl, 6	2.73	0.016	31.34
UCl$_4$ in LiCl (atm. HCl), 750 °C, k_{max} = 10 Å^{-1}	U–O, 0.5[a]	1.79	0.018	34.65
	U–Cl, 6	2.63	0.040	
UCl$_4$ in LiCl, quenched melt, k_{max} = 10 Å^{-1}	U–O, 0.5[a]	1.77	0.010	31.97
	U–Cl, 6	2.69	0.032	
UCl$_3$ in LiCl–BeCl$_2$ (atm. Ar), quenched melt, k_{max} = 11 Å^{-1}	U–Cl, 6	2.92	0.015	27.46
	U–U, 6	5.19	0.016	
UCl$_3$ in LiCl (atm. Ar), 750 °C, k_{max} = 10 Å^{-1}	U–O, 0.5[a]	1.69	0.011	27.88
	U–Cl, 6	2.72	0.050	
UCl$_3$ in LiCl (atm. Ar), quenched melt, k_{max} = 11 Å^{-1}	U–Cl, 6	2.91	0.014	28.88

[a] Oxygen contamination due to partial oxidation of the samples during necessary manipulation prior to exposure to synchrotron radiation from the cyclotron.

of UCl_4 and UO_2Cl_2 (both under HCl atmosphere) in LiCl–$BeCl_2$ eutectic melt results in the melts containing uranium(IV) complexes of essentially identical structure (Table 2).

For uranium complexes in LiCl–$BeCl_2$ melt the U–Cl bond length increases upon melt quenching (as a result of lowering the symmetry of the complex [1,7]), and with decrease in the uranium oxidation state. Similar behaviour was previously observed for uranium in LiCl-based melts [1], and examples of these data are included in Table 2 for comparison. For U(IV) ions, the U–Cl bond length in the LiCl–$BeCl_2$ melt at 380 °C is slightly shorter than in the pure LiCl melt at 750 °C. The same is also true for U–Cl distances in U(VI) complexes in LiCl–$BeCl_2$ and LiCl melts, (Table 2). It is difficult to tell without conducting additional systematic studies whether temperature or melt composition has greater effect on the bond lengths.

The XAS of the melt containing a mixture of U(IV) and U(VI) at 380 °C, obtained upon dissolving UO_2Cl_2 in LiCl–$BeCl_2$ melt under Cl_2 atmosphere, showed the presence of uranyl complexes and associated equivalent chloride ligands (U–Cl distance, 2.56 Å). The U–O distance of 1.72–1.74 Å corresponds to that in the complexes of uranyl ion. The coordination number of 0.5 indicates that only part of uranium was present in the form of uranyl. The uncertainty in coordination numbers determined using EXAFS is normally around 20%. It should also be remembered that in the case of a mixture of several species of a particular element EXAFS analysis gives an averaged picture, often with non-integer coordination numbers. After quenching, the picture has changed and the experimental spectrum is best described by a model with oxygens at 1.74 Å, two chloride ligands at 2.54 Å and four Cl ligands at 2.74 Å. Since the melt contains a mixture of several species of different composition and structure, the values of the coordination numbers obtained from the computer simulation cannot be absolute.

Acknowledgements

We thank the EPSRC for funds for beam time at the Daresbury Synchrotron Radiation Facility. V.A.V. thanks British Nuclear Fuels plc for a Post-doctoral Research Fellowship and for research facilities at Manchester University.

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