Inorg. Chem. **2005**, *44*, 2–4

Inorganic Chemistry
Communication

Uranium Oligomerization in Chloride-Based High Temperature Melts: *In Situ* XAS Studies

Anand I. Bhatt,[†] Erwan du Fou de Kerdaniel,[†,‡] Hajime Kinoshita,[†] Francis R. Livens,[†] Iain May,*,[†] Ilya B. Polovov,[§] Clint A. Sharrad,[†] Vladimir A. Volkovich,*,[§] John M. Charnock,[||] and Robert G. Lewin[⊥]

Centre for Radiochemistry Research, Department of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, U.K., Rare Metals Department, Ural State Technical University, 19 Mira Street, Ekaterinburg 62002, Russia, CCLRC Daresbury Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, U.K., and Nuclear Science and Technology Services, BNFL, Sellafield, Seascale, Cumbria CA20 1PG, U.K.

Received October 5, 2004

In situ EXAFS spectroscopic studies of uranium compounds in high temperature alkali chloride melts indicate the presence of oligomeric species. An investigation into UCl_3 and UCl_4 dissolved in LiCl reveals long range ordering of uranium atoms in the molten state which is not maintained on quenching. Studies of uranium dioxide dissolved in LiCl–KCl eutectic with HCl exhibit long range ordering in both molten and quenched states, and the EXAFS data can be modeled using multiple coordination shells.

Molten salts have many applications in actinide processing and separations. All plutonium electrorefining is currently undertaken in molten salt baths (e.g., equimolar NaCl−KCl). In addition, pyrochemical processes for the electrochemical separation of uranium (and plutonium) from irradiated nuclear fuel have been studied for several years. These processes have been developed to pilot plant scale at ANL, Argonne West, U.S.A., which uses LiCl−KCl eutectic, and at RIAR, Dimitrovgrad, Russia, which is based on NaCl−KCl melts.[1] Current research is focused on the next generation of pyrochemical processes for actinide separations.[2]

The development of electrochemical separation technologies for actinides in molten salts relies on a sound understanding of the key electrochemical processes, i.e., anodic dissolution, cathodic deposition, and electrotransport. An increased awareness of *in situ* actinide speciation could help underpin such electrochemical development. However, probing the actinide coordination environment in high temperature melts is extremely challenging, with a limited number of spectroscopic techniques available.

It might be postulated that simple monomeric chloro complexes dominate $An^{4+/3+}$ and $\{AnO_2\}^{2+}/\{AnO_2\}^{+}$ chemistry in ionic chloride based melts (*i.e.*, $[AnCl_6]^{3-/2-}$, $[AnO_2Cl_4]^{2-/-}$). However, a recent Raman spectroscopic study of $ThCl_4$ in alkali chloride melts indicates the presence of oligomeric species with bridging chlorides.[3] In addition, electronic absorption spectroscopic (EAS) studies indicate the presence of $\{NpO_2\}^{+}/\{UO_2\}^{2+}$ cation/cation interactions in a CsCl melt[4] and $\{UO_2\}^{2+}$ peroxo dimers in a NaCl−CsCl eutectic.[5] These results indicate that simple monomeric cationic complexes may not always be the dominant species.

Previously, we have used *in situ* EAS to study uranium speciation in molten systems,[6] which is able to provide information on oxidation state, but is not a particularly good probe of coordination environment. However, we have also used X-ray absorption spectroscopy (XAS) to probe oxidation state and the coordination environment of Tc and Re in quenched chloride melts at room temperature.[7] Recently, an XAS study of U^{III} in a LiCl−KCl melt at 550 °C has been reported where extended X-ray fine structure (EXAFS) data were collected to an E_{max} of 17.7 keV. However, at high energies the spectra suffer somewhat from low signal-to-

---

* To whom correspondence should be addressed. E-mail: iain.may@man.ac.uk (I.M.); volkovich@dpt.ustu.ru (V.A.V.). Fax: +44 161 275 4598 (I.M.). Phone: +44 161 275 4657 (I.M.).

[†] The University of Manchester.

[‡] Present address: Groupe de Radiochimie, Institut de Physique Nucléaire, Université de Paris-Sud-11, Bat.100, 91406 Orsay, France.

[§] Ural State Technical University.

[||] CCLRC Daresbury Laboratory.

[⊥] Nuclear Science and Technology Services, BNFL.

(1) (a) Laidler, J. J.; Battles, J. E.; Miller, W. E.; Ackerman, J. P.; Carls, E. L. *Prog. Nucl. Energy* **1997**, *31*, 131. (b) Bychkov, A. V.; Vavilov, S. K.; Porodnov, P. T.; Skiba, O. V.; Popkov, G. P.; Pravdin, A. K. *Molten Salt Forum* **1998**, 525.

(2) See, for example: (a) Serp, J.; Konings, R. J. M.; Malmbreck, R.; Rebizant, J.; Scheppler, C.; Glatz, J.-P. *J. Electroanal. Chem*. **2004**, *561*, 143. (b) Uozumi, K.; Iizuka, M.; Kato, T.; Inoue, T.; Shirai, O.; Iwai, T.; Arai, Y. *J. Nucl. Mater*. **2004**, *325*, 34. (c) Serrano, K.; Taxil, P. *J. Appl. Electrochem.* **1999**, *29*, 497.

(3) Photiadis, G. M.; Papatheodorou, G. N. *J. Chem. Soc., Dalton Trans.* **1999**, 3541.

(4) Barbanel', Yu. A.; Dushin, R. B.; Kolin, V. V.; Kotlin, V. P.; Mashirov, L. G.; Nekhoroshkov, S. N. *Radiokhimiya* **2003**, *45*, 253.

(5) Vavilov, S. K.; Porodnov, P. T.; Skiba, O. V. *Rasplavy* **1996**, *5*, 45.

(6) Volkovich, V. A.; Bhatt, A. I.; May, I.; Griffiths, T. R.; Thied, R. C. *J. Nucl. Sci. Technol*. **2002**, Suppl. 3, 595.

(7) Volkovich, V. A.; May, I.; Charnock, J. M.; Lewin, B. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5753.

10.1021/ic048617v CCC: $30.25

noise ratio. As a result, information concerning only the first coordination sphere, which was described as containing 7.3 Cl ligands at a distance of 2.82 Å from uranium, was obtained.[8] XAS can be more readily applied to lower temperature solvent systems, and the coordination environments around $\{UO_2\}^{2+}$ in 1-methyl-3-butylimidazolium hexafluorophosphate and 1-methyl-3-octylimidazolium bis-(trifluoromethanesulfonyl)imide have recently been reported.[9] Clearly, XAS is a useful spectroscopic method that can be applied to understanding uranium speciation and merited further study. Our initial experiments to probe U^{III} and U^{IV} speciation at high temperatures in alkali chloride melts are reported here.

The preliminary melts investigated by XAS[10] were based on LiCl, a weak scatterer of X-rays,[11] and prepared by dissolving UCl_4 or UCl_3 in the molten salt. The resultant melts were then rapidly quenched under an argon atmosphere. The oxidation state of uranium in the melt was confirmed by *in situ* EAS measurements[6] and oxidimetric analysis of quenched samples.[13] High temperature melts containing U^{IV}, and particularly U^{III}, have a high affinity for oxygen.[12] In freshly prepared samples after dissolution of UCl_3 and UCl_4, the oxidimetric analysis showed that the average oxidation state of uranium was 3.1 and 4.0, respectively. The transportation and manipulation of samples meant that trace oxygen contamination was essentially unavoidable, resulting in partial oxidation to $\{U^{VI}O_2\}^{2+}$, and this was taken into account when fitting the EXAFS data. It is recognized that the U−O distance modeled for UCl_3 in LiCl at 750 °C is abnormally short.

The previously prepared, quenched, U-containing samples were held in a horizontal part of an inverted T-shaped silica cell having a path length of 2 or 3 mm and heated in an optical furnace equipped with two beryllium windows. Spectra of the remelted samples (>400 °C) and the quenched solids at room temperature were recorded in transmission mode. The XANES component of the spectra showed that the U L_{III}-energy edge in U^{III}-containing melts had a negative shift of 5.1 eV relative to the edge for U^{IV} experiments, which is consistent with the decrease in Z_{eff}.[14]

Table 1. EXAFS Data[17]

sample	[U] (wt %)	k_{max} (Å^{-1})	occupancy[b]	dist (Å)[c]	$2\sigma^2$ (Å^2)[d]	R
UO_2 exposed to HCl in LiCl−KCl at 450 °C	1.8	8.5	U−O (0.8)	1.84	0.010	37.8
			U−Cl (6)	2.68	0.029	
			U−U (4)	3.74	0.008	
			U−K (6)	4.51	0.003	
UO_2 exposed to HCl in LiCl−KCl, quenched	1.8	9.2	U−Cl (6)	2.62	0.017	36.7
			U−K (6)	3.06	0.019	
			U−U (10)	4.14	0.003	
			U−K (12)	4.36	0.006	
UCl_4 in LiCl at 750 °C[a]	4.5	10	U−O (0.5)	1.79	0.018	34.7
			U−Cl (6)	2.63	0.040	
UCl_4 in LiCl ,quenched[a]	4.5	10	U−O (0.5)	1.77	0.010	32.0
			U−Cl (6)	2.69	0.032	
UCl_3 in LiCl at 750 °C[a]	10.3	10	U−O (0.5)	1.69	0.011	27.9
			U−Cl (6)	2.72	0.050	
			U−Li (12)	3.26	0.057	
UCl_3 in LiCl, quenched[a]	10.3	11	U−Cl (6)	2.91	0.014	28.9

[a] Reference 15. [b] ±20%. [c] ±0.02 Å. [d] $2\sigma^2$ = Debye−Waller factor.

The EXAFS for both UCl_4 and UCl_3 samples (see Supporting Information and Table 1) indicated the first coordination sphere of uranium consists of six Cl^- ligands. When fitting the EXAFS data, oxygen (at U−O distances corresponding to the $\{UO_2\}^{2+}$ group) was required to obtain a good fit. Since U^{III}/U^{IV} were only partially oxidized, the occupancy for oxygen is well below 1. The first shell fitted data would therefore suggest that $[UCl_6]^{3-}$ and $[UCl_6]^{2-}$ dominate U^{III} and U^{IV} speciation, respectively, in both the molten and quenched samples. However, the EXAFS spectra of these melts exhibit high-frequency oscillations at high *k*-values which are not present in the quenched systems, suggesting the possibility of long range ordering of heavy uranium atoms in the molten state.[15] Interestingly, an improved fit can be obtained by incorporating a second coordination sphere of Li cations around $[UCl_6]^{3-}$.

Clearly, there is additional information about U speciation contained in these data, but attempts to fit the full *k*-range data (up to 15 Å^{-1}) have not resulted in any statistically justifiable increase in the number of fitted shells. Previously, EXAFS data have been fitted with long range [U−U] interactions indicative of dimeric and trimeric species,[16] and coupled with the Th oligomeric species proposed in the Raman spectroscopic study of $ThCl_4$ in alkali chloride melts,[3] we postulate that these oscillations are due to long-range ordering of uranium atoms (U−U distances: 3.5−5.5 Å), perhaps together with shells containing alkali cations.

---

(8) Okamoto, Y.; Akabori, M.; Itoh, A.; Ogawa, T. *J. Nucl. Sci. Technol.* **2002**, Suppl. 3, 638.

(9) Visser, A. E.; Jensen, M. P.; Laszak, I.; Nash, K. L.; Choppin, G. R.; Rogers, R. D. *Inorg. Chem.* **2003**, *42*, 2197.

(10) Uranium L_{III}-edge XAS of high temperature melts and quenched samples were recorded in transmission mode on station 9.3 of the CCLRC 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, detuned to 50% of maximum intensity to minimize harmonic generation. The data were collected to E_{max} of 18 keV. The spectra were summed, calibrated, and background subtracted using the Daresbury Laboratory programs EXCALIB, EXBACK, and EXSPLINE. The spectra were simulated using the EXCURV98 program (Gurman, S. J.; Binsted, N.; Ross, I. *J. Phys. C* **1984**, *17*, 143).

(11) Okamoto, Y.; Akabori, M.; Motohashi, H.; Shiwaku, H.; Ogawa, T. *J. Synchrotron Radiat.* **2001**, *8*, 1191.

(12) Griffiths, T. R.; Volkovich, V. A. *J. Nucl. Mater.* **1999**, *274*, 229.

(13) Oxidimetric analysis was performed by dissolving the quenched melt in 10 M H_2SO_4 and oxidizing the uranium present to $\{UO_2\}^{2+}$ with an excess of a standardized solution of NH_4VO_3 in 5 M H_2SO_4. The excess V^V was back-titrated with $(NH_4)_2Fe(SO_4)_2$ in 5 M H_2SO_4 using *N*-phenylanthranilic acid as an indicator.

(14) (a) Hess, N. J.; Weber, W. J.; Conradson, S. D. *J. Alloys Compd.* **1998**, *271−3*, 240. (b) Docrat, T. I.; Mosselmans, J. F. W.; Charnock, J. M.; Whiteley, M. W.; Collison, D.; Livens, F. R.; Jones, C.; Edmiston, M. J. *Inorg. Chem.* **1999**, *38*, 1879.

(15) These LiCl results were initially presented at the International Symposium on Ionic Liquids in Honour of Marcelle Gaune-Escard; Carry le Rout: France, 2003.

(16) See, for example: (a) Allen, P. G.; Bucher, J. J.; Clark, D. L.; Edelstein, N. M.; Ekberg, S. A.; Gohdes, J. W.; Hudson, E. A.; Kaltsoyannis, N.; Lukens, W. W.; Neu, M. P.; Palmer, P. D.; Reich, T.; Shuh, D. K.; Tait, C. D.; Zwick, B. D. *Inorg. Chem*. **1995**, *34*, 4797. (b) Allen, P. G.; Shuh, D. K.; Bucher, J. J.; Edelstein, N. M.; Reich, T.; Denecke, M. A.; Nitsche, H. *Inorg. Chem*. **1996**, *35*, 784. (c) Moll, H.; Geipel, G.; Reich, T.; Bernhard, G.; Fanghanel, T.; Grenthe, I. *Radiochim. Acta* **2003**, *91*, 11.

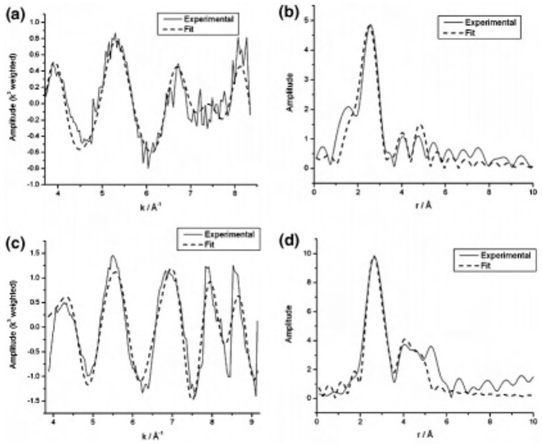

Figure 1. U L_{III}-edge EXAFS spectra of UO_2 in LiCl−KCl eutectic exposed to HCl. Spectra a, with Fourier transform b, were recorded in the molten state {450 °C} while spectra c, with Fourier transform d, were recorded in the quenched state (room temperature).

Our subsequent studies have focused on variations in uranium source, salt type, concentration, and temperature in order to gain a more definitive insight into potential uranium oligomerization. We have discovered that the exposure of UO_2 to HCl in LiCl−KCl eutectic again yields EXAFS data indicative of the presence of long range ordering, although in this case in both the molten and quenched states. The spectra for these samples are presented in Figure 1 (for full *k*-range data see Supporting Information), and all fitted parameters are listed in Table 1. The first coordination sphere can be modeled with six chlorine atoms, with some partial oxidation to $\{UO_2\}^{2+}$ observed in the molten sample.[17] *In situ* EAS results (see Supporting Information) show the majority of the uranium present exists as U^{IV}, while oxidimetric analysis of the quenched sample[13] indicates some oxidation to $\{UO_2\}^{2+}$ (average oxidation state 4.2). The EXAFS spectra for these samples can be fitted by including U−U and U−K distances between 3 and 4.5 Å. The inclusion of these additional shells provides a statistically significant improvement in fit (see Supporting Information). The low uranium concentration within these chloride salts and the observation of uranium EXAFS indicate that this U cluster formation is not merely due to a random homogeneous distribution of uranium throughout the melt.

The different data fits obtained in the molten versus quenched melt samples clearly show that these long-range interactions do alter between solid and liquid states. In the case of the quenched melt, the modeled U−Cl distance in the first coordination sphere (2.62 Å) indicates that the majority of these chlorines, if not all six, are terminally bonded and the interactions with the following coordination sphere predominantly ionic. Solid state structures of uranium dimer complexes exhibit terminal U^{IV}−Cl distances as low as 2.55 Å while bridging U^{IV}−Cl bond lengths range between 2.76 and 2.88 Å.[18] In the molten example, the average U−Cl distances (2.68 Å) are longer than those for the quenched melt which perhaps suggests there are more chlorines acting as bridging ligands. The Debye−Waller factors for all the U−Cl distances modeled are relatively high indicating the possibility of a high degree of thermal motion about the Cl shells, and/or there may be several U−Cl distances from a combination of terminal and bridging Cl ligands that contribute to the average shell. Solid state structures of two-dimensional chloro-bridged $\{UO_2\}^{2+}$ tetramers have U−U distances as short as 3.67 Å[19] whereas the majority of chloro-bridged uranium dimers and trimers have U−U distances between 4.0 and 4.7 Å.[18] Our results therefore perhaps indicate the breakdown of larger oligomeric units on quenching as the shortest U−U distance obtained from the quenched melt data is 4.14 Å while that for the molten sample is 3.74 Å.

In summary, this EXAFS spectroscopic study into uranium chloride dissolution in ionic melts has yielded clear evidence that U speciation is not dominated by simple, monomeric, anionic species, but that clustering can occur. This has implications in electrochemical separation technologies as the efficiency of these processes depends on the mobility of actinide species in the melt. The presence of oligomeric actinide species in molten chlorides means that the actinide diffusion properties, dependent on size and charge, are considerably more complicated. We are currently developing a furnace system that will allow us to undertake XAS measurements using different melts with variable actinide concentrations (through fluorescence measurements), and higher specific radioactivity actinides (Np and Pu). We are also investigating the application of complementary *in situ* Raman spectroscopy measurements.

Acknowledgment. We would like to acknowledge BNFL for funding, the EPSRC/CCLRC for the provision of synchrotron radiation facilities, and INTAS for a fellowship for I.B.P to work at Manchester (Grant 03-55-1453).

Supporting Information Available: EXAFS and UV−vis spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

IC048617V

---

(17) We attribute the presence of $\{UO_2\}^{2+}$ in the UO_2 molten sample, but not the quenched form, to the need for further manipulation of the molten sample at the beamline. After packing the quenched sample under Ar in a drybox, there is no requirement for any manipulation at the beamline.

(18) See, for example: (a) Rebizant, J.; Spirlet, M. R.; Apostolidis, C.; van den Bosch, G.; Kanellakopulos, B. *Acta Crystallogr., Sect. C: Cryst. Struct. Chem. Commun.* **1991**, *47*, 864. (b) Coles, S. J.; Danopoulos, A. A.; Edwards, P. G.; Hursthouse, M. B.; Read, P. W. *J. Chem. Soc., Dalton Trans.* **1995**, 3401. (c) Arliguie, T.; Ephritikhine, M.; Lance, M.; Vigner, J.; Nierlich, M. *J. Organomet. Chem.* **1994**, *484*, 195.

(19) (a) Geras'ko, O. A.; Samsonenko, D. G.; Sharanova, A. A.; Virovets, A. V.; Lipkowski, J.; Fedin, V. P. *Russ. Chem. Bull.* **2002**, *51*, 346. (b) Van den Bossche, G.; Spirlet, M. R.; Rebizant, J.; Goffart, J. *Acta Crystallogr.* **1987**, *C43*, 837.