Spectroelectrochemical Study of Neptunium in Molten LiCl-KCl Eutectic

Ilya B. Polovov[a], Clint A. Sharrad[b], Iain May[b], Vladimir A. Volkovich[a], and
Boris D. Vasin[a]

[a] Department of Rare Metals, Ural State Technical University, 620002 Ekaterinburg, Russia
[b] Centre for Radiochemistry Research, The University of Manchester, M13 9PL Manchester,
United Kingdom

Reprint requests to Dr. I. B. P.; E-mail: polovov@dpt.ustu.ru

Z. Naturforsch. **62a,** 745 – 748 (2007); received June 11, 2007

Presented at the EUCHEM Conference on Molten Salts and Ionic Liquids, Hammamet, Tunisia, September 16 – 22, 2006.

Neptunium behaviour in an LiCl-KCl eutectic melt at 723 K was studied using spectroelectrochemistry. Cathodic reduction of neptunium(IV)-containing melts led to the formation of Np(III) ions and then neptunium metal. Electronic absorption spectra of Np(IV) and Np(III) chloro species in LiCl-KCl melt were recorded and resolved into individual Gaussian bands. The nature of neptunium complex ions in the melt is discussed.

Key words: Neptunium; Chloride Melts; Spectroscopy; Electrochemistry; Spectroelectrochemistry.

1. Introduction

Molten salts have many applications in actinoide processing and separations. Pyrochemical processes for the electrochemical separation of actinoides and fission products from irradiated nuclear fuels have been studied for several years. These technologies have been developed to a pilot plant scale at the Argonne National Laboratory, Argonne West, USA and at the Russian Institute of Atomic Reactors, Dimitrovgrad, Russia. Current research is focused on the next generation of pyrochemical processes for actinoide separations.

The development of safe and reliable separation technologies for actinoides in molten salts relies on a sound understanding of the key electrochemical processes. An increased awareness of *in situ* actinoide speciation could help underpin such electrochemical development. The most useful and direct information concerning coordination properties of actinoides in molten salts can be obtained from electronic spectroscopy. Combination of electrochemistry and spectroscopy in one spectroelectrochemical cell provides unambiguous information concerning the speciation of the studied element.

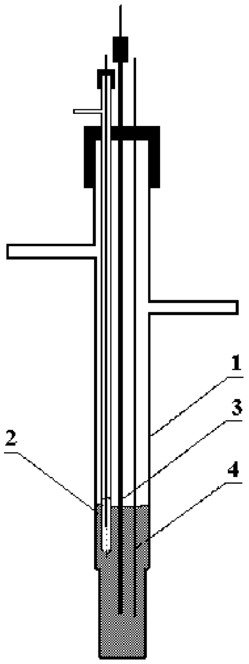

Fig. 1. Experimental spectroelectrochemical cell. 1, Silica optical cell; 2, chlorine reference electrode; 3, quartz capillary tube for chlorination; 4, glassy-carbon working electrode.

2. Experimental

The experiments were carried out in a standard 1 cm silica optical cell attached to a silica tube (20 mm i. d.) with two side-arms (Fig. 1). A glassy-carbon rod was used as working electrode. The other glassy-carbon or chlorine electrode in a quartz sheath served both as a counter and quasi-reference electrode and was separated from the bulk of the melt by a diaphragm.

The progress of electrode reactions was followed by in situ electronic spectroscopy and voltammetry measurements. Spectroscopic measurements were performed using a fibre optic spectrophotometer Avantes Avaspec-2048-2 with an Avalight DH-S deuterium-halogen light source. A PAR/EG&G Model 263A potentiostat/galvanostat was used to control the current passed through the cell and to monitor the red-ox potential of the working electrode. The current was set to 5 mA.

Neptunium(IV)-containing samples were prepared by chlorinating hydrated neptunium(IV) oxide/chloride by hydrogen chloride in the melt. The neptunium stock solution in 1 M HNO_3 had a neptunium(V) concentration of 0.1 mol/l. An aliquot of this solution (containing 20 mg of ^{237}Np) was mixed with the stoichiometric amount of a 6 M NaOH solution to precipitate $NpO_2OH \cdot xH_2O$. The samples were centrifuged, the supernatant liquid decanted and the remaining solid washed with distilled water. This procedure was repeated once more, and the resulting solid was then dissolved in 1 M HCl to form NpO_2Cl. Several drops of HI solution (57 wt%) were added to this solution to reduce Np(V) to Np(IV). The solution was evaporated to near dryness under a heat lamp. The residual was diluted with water, and the stoichiometric amount of 6 M NaOH was added to completely precipitate $Np(OH)_4$. The mixture was centrifuged, the supernatant liquid removed and the remaining solid washed with distilled water. The sample was centrifuged and the liquid decanted. The solid precipitate was dissolved in 1 M HCl to form an olive green solution of $NpCl_4$ (the completeness of the reduction was confirmed by UV-vis-NIR spectroscopy). This solution was transferred into the high temperature spectroscopy cell. The cell was sealed and purged with argon. The solution was evaporated to dryness, giving the orange, solid $NpCl_4$. The cell was then kept under vacuum with gentle heating for several hours to remove traces of moisture from the neptunium chloride.

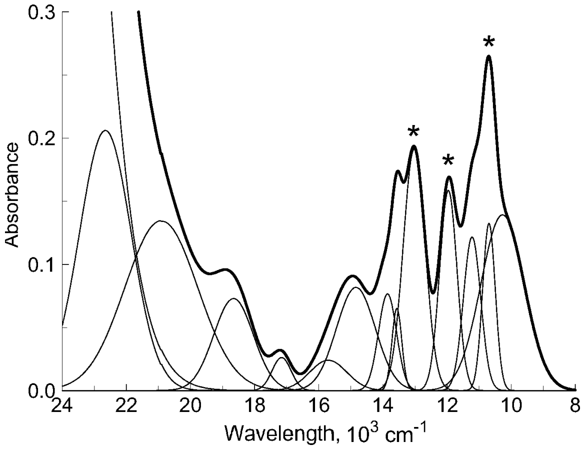

Fig. 2. Spectrum of Np(IV), $[NpCl_6]^{2-}$, in an LiCl-KCl melt at 723 K. Hypersensitive bands are marked with *. Neptunium(IV) concentration, ca. 0.015 mol/l.

All experiments were performed in an LiCl-KCl eutectic (m. p. 633 K). Solid eutectic was added to the spectroscopic cell containing prepared neptunium chloride in an inert atmosphere glove box, closed with a stopper, transferred into an optical furnace and heated to 723 K under argon. Hydrogen chloride was bubbled through the melt for 1 h to convert any remaining oxide-containing neptunium species into chlorides.

3. Results and Discussion

The recorded spectrum of the Np(IV)-containing chloride melt is shown in Figure 2. The spectral profile agrees very well with the data reported by Gruen et al. [1] and Barbanel' et al. [2]. The major bands situate at 530, 585, 665, 740, 770, 837 and 936 nm and correspond to the hexa-coordinated chloride complexes of neptunium(IV), $[NpCl_6]^{2-}$.

By resolving the experimental spectrum into individual overlapping Gaussian bands, Fig. 2, it was possible to detect some hidden absorption bands and estimate the energies of the corresponding electronic transitions in the chloride ligand environment. The results of the resolution of the $[NpCl_6]^{2-}$ spectrum are summarized in Table 1.

The obtained spectroscopic picture was compared with the energy levels diagram [3]. Neptunium(VI) has f^3 electronic configuration, and the ground level is $^4I_{9/2}$. Using the literature data concerning neptunium coordination in molten chlorides [3] and the results of our previous EXAFS spectroscopy measurements of U(III), also having f^3 cofiguration, in an

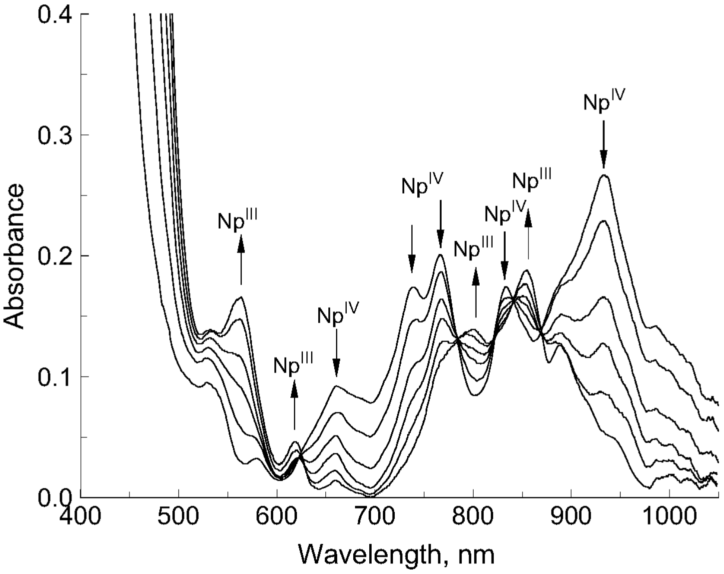

Fig. 3. Spectra recorded during electrochemical reduction of Np(IV) to Np(III) in an LiCl-KCl eutectic melt at 723 K. Initial concentration of neptunium(IV), ca. 0.015 mol/l; total time of reduction, 1280 s; current, 5 mA.

Table 1. Parameters of individual absorption bands in a resolved $[NpCl_6]^{2-}$ spectrum.

Energy, cm^{-1}	Half-height width, cm^{-1}	Relative intensity, %
10273	1591	68.3
10697	465	64.4
11225	647	60.1
11969	634	77.7
13036	807	93.7
13574	357	31.6
13864	635	35.7
14837	1544	38.5
15620	1518	11.1
17181	685	12.6
18677	1449	34.1
21262	3057	78.9
22710	1809	100.0

(Li-K)Cl melt at 723 K [4], we can conclude that neptunium(IV) in an LiCl-KCl eutectic forms octahedrally coordinated complex $[NpCl_6]^{2-}$ ions.

It is well known that the task of assigning all resolved Gaussian bands to individual f-f electronic transitions (including their vibronic components) cannot be solved due to the high number of Stark's and *J* levels. However, most intense, so-called "hypersensitive" transitions, can be assigned [5].

According to the basic principle of determining hypersensitive transitions ($\Delta J = 2$) and the energy level diagram, there are two major hypersensitive transitions in the studied wavelength range, $^4I_{9/2} \rightarrow {}^4F_{5/2}$ and $^4I_{9/2} \rightarrow {}^4G_{5/2}$. For Np(IV) they are situated at 10000 and 11800 cm^{-1}, respectively. Taking into account the "blue" shift of the peaks resulting from the

Table 2. Parameters of individual absorption bands in a resolved $[NpCl_6]^{3-}$ spectrum in an LiCl-KCl melt at 723 K.

Energy, cm^{-1}	Half-height width, cm^{-1}	Relative intensity, %	Positions of Np(III) bands in CsCl melt at 973 K (data from [2])
10740	628	40.7	10420
11173	405	65.5	11100 (shoulder)
11672	515	100.0	11650
12225	999	71.0	12620
12947	1077	66.9	13140
15124	636	9.4	15480
16176	638	31.3	16100
17660	1157	88.4	
18778	1763	75.4	

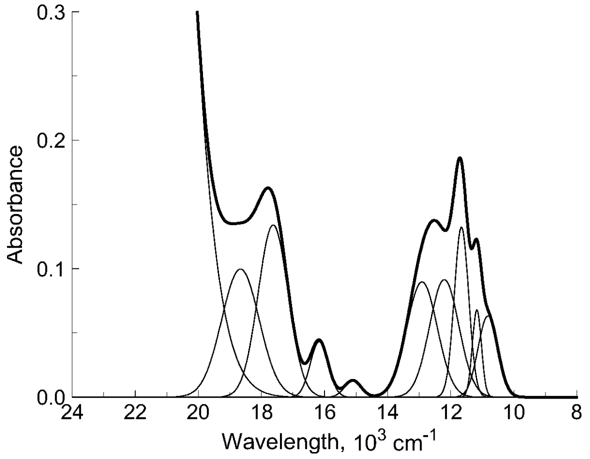

Fig. 4. Spectrum of Np(III), $[NpCl_6]^{3-}$, in an LiCl-KCl melt at 723 K.

nephelauxetic effect, the absorption bands at 10200–11200 cm^{-1} and ca. 11970 cm^{-1} can be reliably attributed to these hypersensitive f-f transitions and associated fine structure bands. Another intensive absorption peak at ca. 13030 cm^{-1} is likely associated with a $^4I_{9/2} \rightarrow {}^4G_{7/2}$ electronic transition which satisfies two additional requirements for hypersensitive transitions ($\Delta L = 2$ and $\Delta S = 0$). The nature of other peaks is not obvious. For example, at relatively high energies (wavenumbers) bands arising from f-d electronic transitions are also possible.

The progress of neptunium(IV) electroreduction was followed by in situ electronic absorption spectroscopy. As can be seen in Fig. 3 the intensities of the bands corresponding to Np(IV) decrease. At the same time new peaks at 565, 790, 660, 800, 855 and 890 nm appear and grow. There are 5 isosbestic points at 625, 785, 822, 842 and 870 nm (Fig. 3), indicating that the total concentration of neptunium in the melt remained constant during the neptunium(IV) electoreduction: $[NpCl_6]^{2-} \rightarrow [NpCl_6]^{3-}$. The spectral profile of the final obtained spectrum is typical of the neptunium(III) chloro complex [1–3, 6]. After complete conversion of Np(IV) to Np(III) the electrolysis was continued and the intensity of the Np(III) spectrum began to decrease in the entire wavelength range due to reduction of Np(III) ions to neptunium metal.

The spectrum attributed to Np(III) was also resolved into individual Gaussian bands (Fig. 4, Table 2). Table 2 also lists Np(III) band positions in a CsCl-based melt at 973 K (after Barbanel' et al. [2]), included for comparison. Np(III) spectra have also been previously recorded in an LiCl-KCl melt at 873 K [1]. The spectra reported in the literature [1, 2] are very similar to the spectrum recorded here thus confirming that the reduction of Np(IV) went to completion. To our knowledge this is the first time the spectrum of Np(III) was measured in an LiCl-KCl melt at 673 K.

Neptunium(III) has f^4 electronic configuration with $^5I_4$ ground state. The energies of the spectral bands were compared with the energy level diagrams [3]. Unfortunately the only hypersensitive band $^5I_4 \rightarrow {}^5I_6$ expected for the f^4 configuration is out of the studied wavelength range. Unambiguously assigning resolved Gaussian bands to specific electronic transitions is a complicated task and requires performing additional theoretical calculations and modelling.

4. Summary

The behaviour of neptunium chloro species in an LiCl-KCl eutectic melt at 723 K was studied for the first time, using spectroelectrochemistry. Neptunium(IV) chloride dissolves in the LiCl-KCl melt producing $[NpCl_6]^{2-}$ ions. Electrochemical reduction of Np(IV) on a glassy-carbon electrode results in the formation of $[NpCl_6]^{3-}$ ions and then leads to the deposition of neptunium metal. Electronic absorption spectra of Np(IV) and Np(III) complex chloride ions were measured between 400 and 1100 nm and resolved into individual overlapping bands.

Acknowledgements

I. B. P. thanks INTAS (Grant No. 03-55-1453) for financial support.

[1] D. M. Gruen, S. Fried, P. Graf, and R. L. McBeth, in: Proceedings of the 2nd International Conference on Peaceful Uses of Atomic Energy, U.N., Geneva 1958, p. 112.

[2] Yu. A. Barbanel', V. P. Kotlin, V. V. Kolin, and G. P. Chudnovskaya, Sov. Radiochimiya **17**, 929 (1975).

[3] Yu. A. Barbanel', Coordination Chemistry of f-Elements in Melts, Energoatomizdat, Moscow 1985 (in Russian).

[4] V. A. Volkovich, I. May, C. A. Sharrad, H. Kinoshita, I. B. Polovov, A. I. Bhatt, J. M. Charnock, T. R. Griffiths, and R. G. Lewin, in: Recent Advances in Actinoide Science (Eds. R. Alvarez, N. D. Bryan, I. May), RSC Publishing, London 2006, p. 485.

[5] D. E Henry, R. L. Fellows, and G. R. Choppin, Coordinat. Chem. Rev. **18**, 199 (1976).

[6] V. V. Kolin, Yu. A. Barbanel', V. P. Kotlin, A. N. Smirnov, A. A. Lumpov, and Yu. I. Gavrish, Sov. Radiochimiya **26**, 525 (1984).