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Contribution to the knowledge of the electrochemical properties of actinides in non-aqueous media

III. The reduction of tetravalent thorium and tetravalent neptunium in various organic solvents

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Abstract

The electrochemical behaviours of both Th(IV) and Np(IV) are investigated in different organic solvents at room temperature and at 400 K in dimethylsulfone ($DMSO_2$) and hexamethylphosphoramide. A four-electron transfer is the characteristic of tetravalent thorium reduction while the corresponding neptunium species is reduced to the metal in two steps where Np(III) is the transient species. The reactions are complicated by additional kinetic phenomena. Neptunium metal is gained with Cs_2NpCl_6 as feed material by reduction on a Hg-pool cathode in acetonitile (current yield, about 7%) while the yield drops to 0.4% in $DMSO_2$.

Keywords: Electrochemical properties; Actinides; Organic solvents

1. Introduction

In two previous papers in this journal [1,2], we compared the electrochemical properties of uranium in various organic media and it became evident that new data about the actinide elements have to be gathered in these solvents.

As far as the electrochemical behaviour of neptunium is concerned, little information is available from experiments carried out in organic liquids [3–6].

Only fragmentary data exist about thorium; they are based on classical polarography with a dropping-mercury electrode [6].

From a theoretical point of view, the electrochemical reduction of Th(IV) to metallic Th would possibly proceeds in two steps involving either Th(II) [6] or Th(III) since the calculated value $E°$ (Th(IV)/Th(0)) = −1.8 V [7] is not too far from the value calculated by Miles [7] (charge transfer spectra data) for the reaction $Th^{4+} + e = Th^{3+}$, i.e. −2.4 V. In turn, if we consider now $E°$ (Th^{4+}/Th^{3+}) = −3.7 V as calculated with Nugent's correlation function a serious gap appears [7]. Up to now, only tetravalent thorium has been characterized in aqueous and organic solutions; in molten salts media, the existence of Th^{2+} seems matter of controversy [7]. We intend to add some data about the hypothetical transient species Th(III) or Th(II).

2. Experimental details

The experimental procedure has been described in [1,2]. The following solvents were considered: acetonitrile (AN); dimethylformamide (DMF); dimethylsulfoxide (DMSO); dimethylsulfone ($DMSO_2$); formamide (FA); hexamethylphosphoramide (HMPA); propylene carbonate (PC).

Anhydrous $ThCl_4$ and Cs_2NpCl_6 [8] are used as the feed materials. $ThCl_4$ is soluble at room temperature in the range 10^{-3}–10^{-2} M in DMSO, PC, HMPA, FA, AN in the presence of a conducting salt (LiCl or

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$LiClO_4$, 0.1 M) while it dissolves immediately in $DMSO_2$ at 400 K without the addition of a conducting salt. In the presence of a conducting salt, Cs_2NpCl_6 is soluble in $DMSO_2$ (400 K) and HMPA (298 K) but in the other solvents CsCl precipitates.

In most of the measurements, the indicator electrode (Pt, W or glassy carbon) has to be withdrawn from the cell after each electrochemical scan and cleaned with either dry acetone or AN in the glovebox; this method is required to obtain reproducible measurements.

All the potentials are referred to a large-area (about $10\ cm^2$) platinum electrode that we consider a quasireference in each solution.

3. Results

Only the most characteristic results are reported; comparisons with the behaviour of uranium rests either on our previous papers [1,2] or on side experiments carried out at the same time with Cs_2UCl_6. When possible, the reduction of Np^{4+} in each solvent was successively investigated by several transient techniques, namely cyclic voltammetry (CV), normal pulse polarography (NPP), differential pulse polarography (DPP), and chronoamperometry (CA) with sampled polarography (SP), and also by controlled potential electrolysis (CPE).

As usual, the results are discussed according to the methods used in the classical textbook by Bard and Faulkner [9] and the review by Nicholson and Shain [10].

3.1. Behaviour of $ThCl_4$

3.1.1. Molten dimethylsulfone (400 K)

At 400 K, the solution of $ThCl_4$ (2.6×10^{-2} M) is stable in the presence of LiCl (2.5×10^{-1} M) as a conducting salt. One ill-defined reduction wave is always obtained in CV experiments while an inverse oxidation peak is observed on reversal (Fig. 1). The shape of this peak ($\overleftarrow{E}_p = +0.13$ V) suggests the anodic stripping of a metal deposited on an inert electrode. The weak pre-peak on reversal ($\overleftarrow{E}_p \approx -0.18$ V) would then correspond to the dissolution of the first layers of deposited thorium.

We tentatively consider that the reduction of Th(IV) to metal proceeds in one step with a four-electron transfer as for the (Li–K)Cl eutectic at 723 K [11]. The ill-shaped reduction peak does not allow further conclusions.

In CPE, a mixture of thorium metal, thorium oxide and organic products is precipitated onto the cathode (Pt) when the working potentials range from −0.59 V down to −0.65 V. When $E_c = -0.55$ V, the presence of ThO_2 is no longer observed but the current yield for the deposition of the pure metal is uninteresting, i.e. about 0.2%.

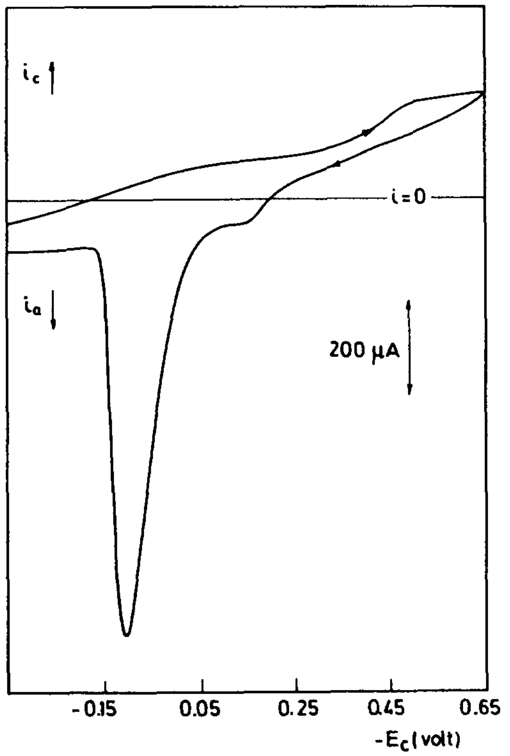

Fig. 1. Voltammetric reduction of $ThCl_4$ (2.6×10^{-2} M) in molten $DMSO_2$ at 400 K (Pt cathode; $v = 0.1\ V\ s^{-1}$; 0.25 M LiCl).

3.1.2. Dimethylsulfoxide, propylene carbonate and hexamethylphosphoramide

In these three solvents, only irreproducible electrochemical signals (CV, NPP and DPP) were evidenced.

3.2. Behavior of Cs_2NpCl_6

It appeared from preliminary experiments that tetravalent neptunium may be oxidized by reaction with some of the usual conducting salts containing a ClO_4^- anion, e.g. $LiClO_4$, Et_4NClO_4 and But_4NClO_4; in these cases the initial green color of the Np(IV) solutions turns to dark green and then to brown within 5 h at room temperature.

In HMPA at 400 K, tetravalent neptunium slowly reacts with the solvent, giving NpO_2^+ as demonstrated by voltammetry.

A plausible reaction scheme could be

$$2R_3PO + Np^{4+} + 2Cl^- \rightarrow R_3P + R_3PCl_2 + NpO_2^{2+}$$

with R_3P as hexamethylphosphorous triamide or $[(CH_3)_2N]_3P$. This reaction does not proceed at room temperature.

3.2.1. *Hexamethylphosphoramide*

As has been evidenced with Cs_2UCl_6 in a previous paper [1] in this series, adsorption phenomena are drastically hampered at 400 K and therefore electrochemistry is easier to understand at this temperature. All the measurements are carried out within 5 h after dissolution of Cs_2NpCl_6 in the solvent.

3.2.1.1. Cyclic voltammetry. Two well-defined reduction peaks appear on the cathodic scan ($\vec{E}_{p1} = -1.240$ V; $\vec{E}_{p2} = -1.990$ V) at 50 mV s^{-1} while no peak is defined on reversal (Fig. 2). As in the case of uranium [1], we consider that the reduction of Np^{4+} is irreversible and proceeds according to a two-step mechanism

$$Np^{4+} + e \rightarrow Np^{3+}\,, \quad Np^{3+} + 3e \rightarrow Np(0)\,.$$

Complementary investigations of the first wave lead to the conclusion that additional kinetic phenomena (coupled chemical reactions) are present.

(1) The plot of the peak current i_p against the square root of the voltage scan speed ($v^{1/2}$ expressed in $V^{1/2}\,s^{-1/2}$) is linear but does not intercept the origin as predicted from the following equation for an irreversible charge transfer reaction:

$$i_p = 0.496n(\alpha n_a)^{1/2}F^{3/2}R^{-1/2}T^{-1/2}AD^{1/2}Cv^{1/2} \qquad (1)$$

where α is the electrochemical transfer coefficient ($0.1 \leqslant \alpha \leqslant 0.9$), n the number of electrons in the electrode process, n_a the number of electrons in the rate-determining step and A (cm^2) the indicator electrode surface. The diffusion coefficient D is given in square centimetres per second and the concentration C in moles per cubic centimetre.

(2) The peak current function $i_p/v^{1/2}$ decreases when v varies from 0.02 to 0.1 V s^{-1} and becomes rather constant from $v = 0.1$ to 0.5 V s^{-1}. When the charge transfer is irreversible without any effect of a coupled chemical reaction, $i_p/v^{1/2}$ remains always independent of v.

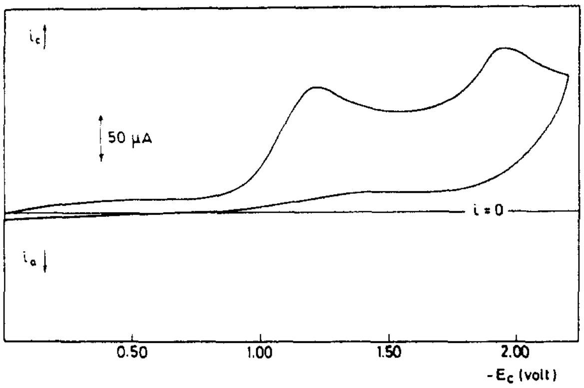

Fig. 2. Voltammetric reduction of Cs_2NpCl_6 (3×10^{-2} M) in HMPA at 400 K (graphite cathode; $v = 0.05$ V s^{-1}; 0.1 M $LiClO_4$).

Nevertheless, the features (1) and (2) are unsuitable for defining a precise mechanism taking into consideration kinetic phenomena for the reduction $Np^{4+} + e \rightarrow Np^{3+}$. No precise information was gained from the analysis of the second wave for this wave is too sensitive to the kinetic parameters of the first wave [10].

3.2.1.2. Chronoamperometry. From CA experiments it is found that the evolution of the current $i(t)$ with time t at constant potential is described at low overvoltages according to:

$$i(t) = nFACk_f\left(1 - \frac{2Ht^{1/2}}{\Pi^{1/2}}\right) \qquad (2)$$

with $H \approx 1/D^{1/2}\,(k_f - k_b)$ where k_f and k_b are the rate constants for the forward and the backward reactions respectively. Graphic extrapolations of the $i(t)$ values to zero time at low overvoltages allow the determination of k_f according to

$$k_f \approx \frac{i(0)}{nFAC} \qquad (3)$$

where $i(0)$ is the current for $t = 0$ (Fig. 3). We find that $k_f \approx 1 \times 10^{-4}$ cm s^{-1} for $E_c = -0.90$ V and that $k_f \approx 2 \times 10^{-4}$ cm s^{-1} for $E_c = -1.00$ V; these numerical values are in reasonable agreement with the irreversible process proposed from CV measurements.

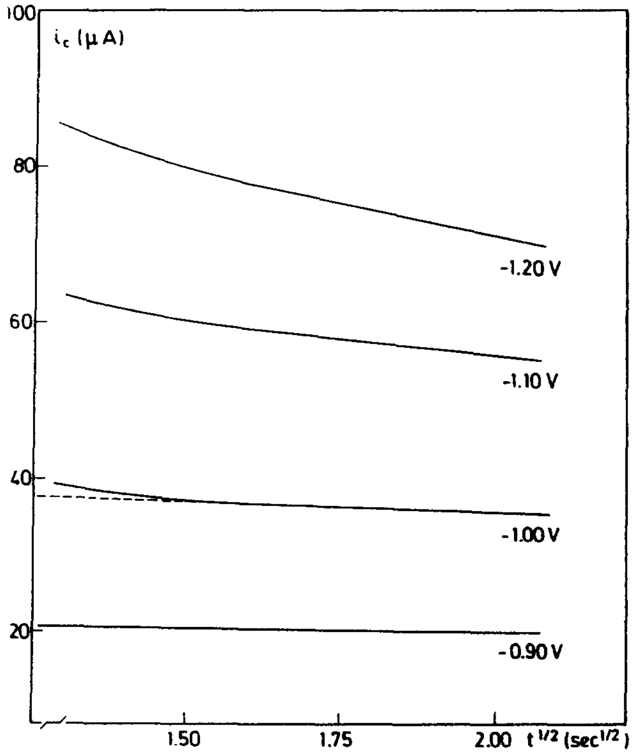

Fig. 3. Plots of the chronoamperometric current $i = f(t)$ against $t^{1/2}$ for the reduction $Np^{4+} + e \rightarrow Np^{3+}$ in HMPA at 400 K (graphite cathode; 3×10^{-2} M Cs_2NpCl_6; 0.1 M $LiClO_4$.)

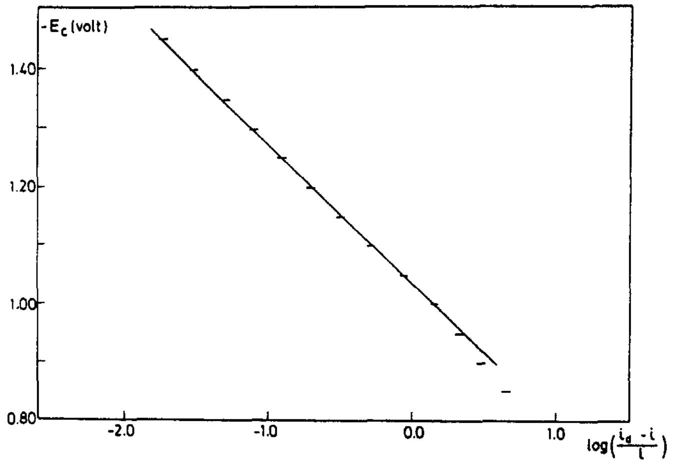

Fig. 4. Sampled polarogram ($t = 4$ s) for the reduction $Np^{4+} + e \rightarrow Np^{3+}$ in HMPA at 400 K (conditions as in Fig. 3).

Sampled polarograms (Fig. 4) are set up from chromoamperometric curves as described earlier in this journal [1]. By this technique, each polarogram is sampled at fixed times (2, 3, 4 or 5 s), so leading to more precise wave shapes. The first wave evidenced in CV is described by the following classical Heyrovsky–Ilkovic equation for an irreversible process when the reduced species (Np^{3+}) is soluble:

$$E = E^{1/2} + \frac{2.3RT}{\alpha nF}\log\left(\frac{i_d - i}{i}\right) \tag{4}$$

where i_d is the limiting current. From the experimental value of the slope $\delta E/\delta[\log(i_d - i)/i]$ we calculate $\alpha n = 0.33 \pm 0.05$. If we accept $n = 1$ for the reaction $Np^{4+} + e \rightarrow Np^{3+}$, $\alpha = 0.33 \pm 0.05$. This value is in good agreement with the accepted values for $\alpha(0.1 \leq \alpha \leq 0.9)$ and more frequently $0.3 \leq \alpha \leq 0.7$. The latter technique confirms that the reduction of tetravalent neptunium is an irreversible reaction.

In the same solvent at 298 K, two additional ill-defined adsorption peaks are observed and the reduction of the tetravalent species proceeds also in two steps.

3.2.1.3. Controlled potential electrolysis. When the cathodic potential is fixed between −1.90 and −2.15 V, the electrode is covered by black crusts containing neptunium but the presence of Np metal was impossible to ascertain.

3.2.2. Dimethylsulphone

A very similar work has been achieved in $DMSO_2$ at 400 K.

3.2.2.1. Cyclic voltammetry. The voltammetric reduction corresponds to three waves (I, II and III) of apparent increasing intensities and to a large ill-defined current on reversal (Fig. 5, lower curve).

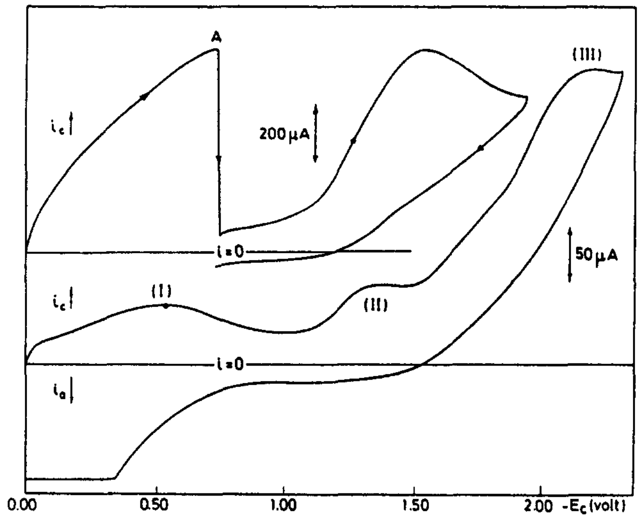

Fig. 5. Voltammetric reductions of Cs_2NpCl_6 (2×10^{-2} M) in molten $DMSO_2$ at 400 K (0.1 M LiCl): upper curve, Pt cathode, $v = 0.050\ V\ s^{-1}$; lower curve, graphite cathode, $v = 0.050\ V\ s^{-1}$.

The first wave matches an adsorption region as demonstrated by DPP. The second wave is investigated as follows. The voltage scan is stopped at the potential A, so allowing the current to decay until a constant current (residual current) is stabilized, and then the scanning of the second wave is continued in turn. After this break the second wave is perfectly shaped and reproducible (Fig. 5, upper curve). We consider that this wave would then correspond to $Np^{4+} + e \rightarrow Np^{3+}$. As expected in the case of an irreversible transfer, i_p is proportional to $v^{1/2}$ (Eq. (1)) and intercepts the origin but the current function $i_p/v^{1/2}$ shows an irregular dependence from v. This denotes additional kinetic effects but no theoretical scheme fits these experimental features [10].

The second wave is not reproducible either in peak potential or in peak current; we tentatively propose that the reduction of Np^{3+} into metal occurs in this potential region.

3.2.2.2. Chronoamperometry. The evolution of the current $i(t)$ is a linear function of $t^{1/2}$ at low cathodic potentials. From Eq. (3) we calculate that $k_f \approx 5 \times 10^{-5}\ cm\ s^{-1}$ for $E_c = -1.10$ V and $k_f \approx 1 \times 10^{-4}\ cm\ s^{-1}$ for $E_c = -1.15$ V assuming that $n = 1$. The values are consistent with the irreversible process evidence from CV curves.

SP confirms the data gained by previous techniques. As in HMPA the reduced species (Np^{3+}) is soluble and the electrochemical transfer coefficient α equals 0.40 ± 0.05 (Eq. (4)). NPP is in reasonable agreement with SP; α is found to be equal to 0.6 ± 0.1 but we prefer the SP value for the reasons stated above.

3.2.2.3. Controlled potential electrolysis. We propose to consider that Np^{4+} is reduced to neptunium metal in two steps but the presence of the metal is not demonstrated by the electroanalytical techniques.

In CPE, the potential of the Pt cathode was fixed between −2.5 and −2.7 V, i.e. in the potential region where Np metal is supposed to be deposited. A black powdery material is precipitated after 22 h electrolysis. The presence of ^{237}Np is ascertained by α spectroscopy but neither Np metal nor NpO_2, $NpCl_3$ and $NpCl_4$ are evidenced by X-ray diffraction. The cathode reduction of the solvent probably impedes Np metal deposition on an hour scale.

With a mercury pool as a cathode, the potential was fixed at −2.7 V; 240 C were involved in this electrolysis. In these conditions, electrodeposited neptunium metal is amalgamated, and side reactions between metal and cathodic decomposition products of the solvent are avoided. The current yield remains nevertheless insignificant (0.4%) but the presence of amalgamated metal confirms the validity of the reduction scheme as above described.

3.2.3. Dimethylformamide

Two well-defined waves appear on the direct cathodic scan and no oxidation peak is observed on reversal (Fig. 6). When the scan is reversed after $\vec{E}_{p1}$ (−1.250 V at $v = 50\,mV\,s^{-1}$) no oxidation peak is observed. The two reactions are irreversible. Between these two peaks, the voltammograms are somewhat distorted. If the sweep is stopped before the second wave (arrow in Fig. 6) in order to allow the current to decay before scanning $\vec{E}_{p2}$, the odd region is still observed but the second wave fits the expected shape for a classical voltammogram well. By comparison with the behaviour of Cs_2UCl_6 and UCl_3 in the same solvent [12] we consider that Np^{4+} reduces in two steps and that transient insolubility of the trivalent species causes the voltammogram to distort. On the basis of the usual diagnostic criteria as discussed above, we also depict the reduction of Np^{4+} as a two-step reaction where additional phenomena impede the complete characterization of the system.

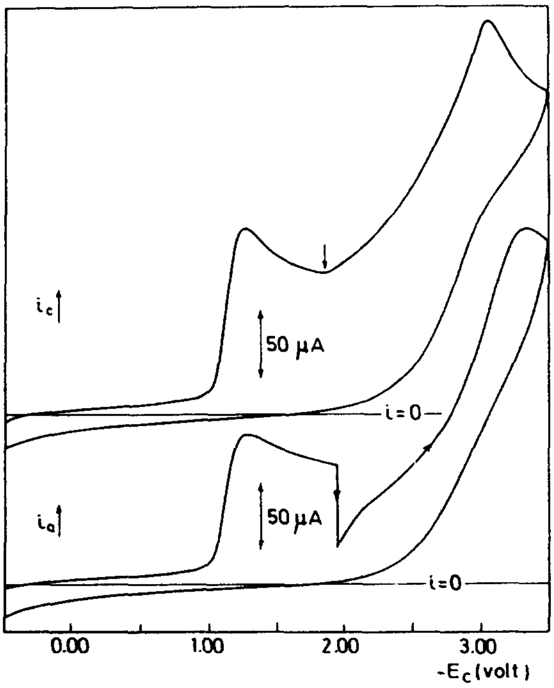

Fig. 6. Voltammetric reductions of Cs_2NpCl_6 (2.5×10^{-2} M) in DMF at 298 K (graphite cathode; $v = 0.05\ V\,s^{-1}$; 0.1 M LiCl).

By SP we find that $\alpha = 0.35 \pm 0.05$ for the reaction $Np^{4+} + e \rightarrow Np^{3+}$ and the following values of k_f are obtained from CA experiments: $k_f \approx 4 \times 10^{-6}\ cm\,s^{-1}$ at $E_c = -1.00$ V and $k_f \approx 8 \times 10^{-6}\ cm\,s^{-1}$ at $E_c = -1.05$ V. The later data confirm the irreversibility of the first electron transfer.

We failed to prepare macroscopic amounts of Np metal by CPE when the cathodic potentials were set up between −3.0 and −3.5 V. Np compounds were obtained (current yield, 0.8%) together with decomposition products of the solvent.

3.2.4. Acetonitrile

The reduction of Np^{4+} is characterized in CV by two ill-defined but rather reproducible waves (Fig. 7).

On the contrary to other solvents, the shape of the complete voltammogram seems to depend on Np^{4+} concentration. With $[NP^{4+}] = 4 \times 10^{-2}$ M, the first wave becomes unshaped but the second peak is well defined ($\vec{E}_{p1} = -1.5$ V) and followed by a hump ($\vec{E}_{p2} \approx 1.7$ V) before the solvent reaction (Fig. 7). The peak observed on reversal disappears when the scan is reversed (Fig. 7, curve (R)). This probably corresponds to the deposition of metallic neptunium in the potentials range of the second peak; the metal would be deposited in successive layers and the anodic

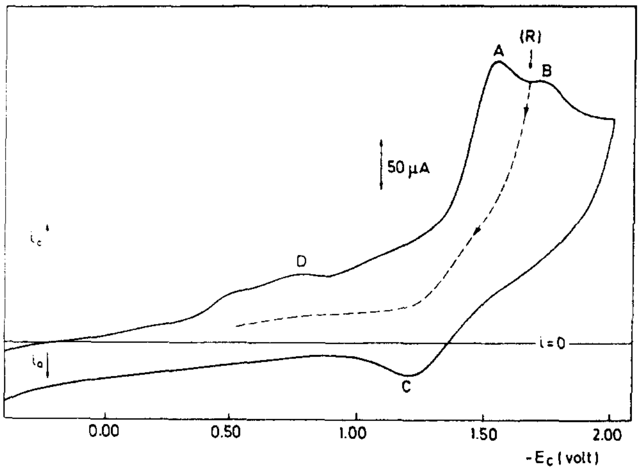

Fig. 7. Voltammetric reduction of Cs_2NpCl_6 (4×10^{-2} M) in AN at 298 K (Pt cathode; $v = 0.05\ V\,s^{-1}$; 0.1 M $LiClO_4$).

stripping of the last of these layers would be responsible for the weak peak on reversal at $E_p \approx -1.22$ V: $Np^0 \rightarrow Np^{3+} + 3e$.

Here again we can tentatively propose a reaction scheme $Np^{4+} + e \rightarrow Np^{3+}$, $Np^{3+} + 3e \rightleftharpoons Np^0$, with partial reversibility in the second step as in the case of uranium [13]. The irreversibility of the first wave is confirmed by CA experiments: $k_f \approx 1 \times 10^{-6}$ cm s^{-1} for $E_c = -0.5$ V as deduced from Eq. (3).

The deposition of Np metal was never achieved on Pt or graphite cathodes; only black deposits containing neptunium were secured in the potential range from −1.3 to −1.9 V. Metallic neptunium is amalgamated into a mercury-pool cathode at $E_c = -1.8$ V; the current yield for Np deposition is about 7% when 125 C are involved with a 6 h electrolysis.

3.2.5. Formamide

Contrary to the above-quoted solvents, FA is a protonic liquid with a dielectric constant of about 110 at ambient temperature. Liquids of high dielectric constant are the best solvents for ionic compounds but the cathodic window of a protonic solvent is restricted because of the protons reduction at low overvoltages. In the case of FA, the anodic and cathodic products issuing from the electrochemical reactions of the solvent are gaseous and will react only to a small extent with the actinide metal to be prepared.

These considerations have been confirmed in a parallel work dealing with electrodeposition of lanthanide metals (Dy and Sm) in FA [14].

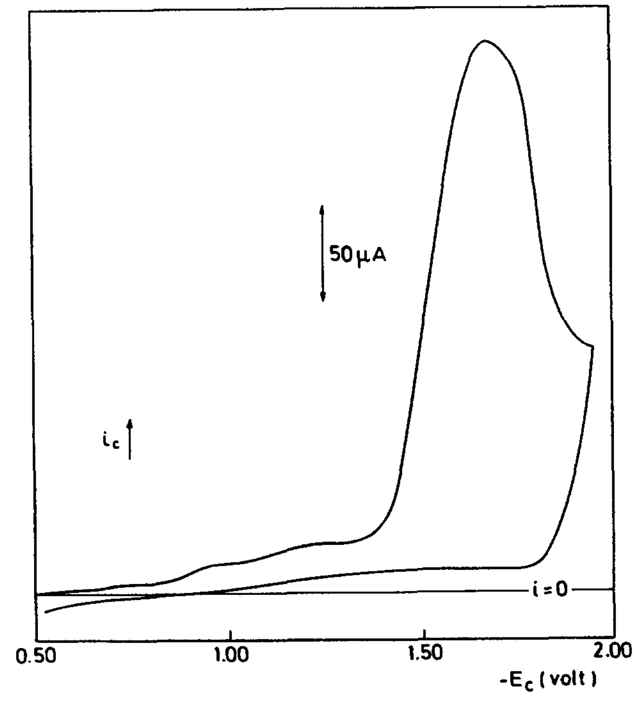

Fig. 8. Voltammetric reduction of Cs_2NpCl_6 (2.5×10^{-2} M) in FA at 298 K (Pt cathode; $v = 0.02$ V s^{-1}).

Cs_2NpCl_6 is soluble in FA, as also is Cs_2UCl_6. For $[Np^{4+}] = 2.5 \times 10^{-2}$ M no conducting salt is required to reach a flat base line in CV, thus denoting the good conductivity of the medium.

In CV experiments, one well-shaped wave is observed before the reduction of the solvent (Fig. 8) on a glassy carbon electrode with $v = 10$ or 20 mV s^{-1}; at higher speeds the wave flattens and is no longer defined at 100 mV s^{-1}.

The shape of this single wave seems to depict the presence of two merged steps but other techniques (NPP and DPP) failed to confirm this observation. In the same solvent, tetravalent uranium is also characterized by one peak on direct scan and no peak on reversal [12].

The solution is stable within 3 h (298 K).

CPE with $E_c \approx -1.7$ V produces a black deposit containing neptunium but it was impossible to demonstrate in the presence of metal. The current yield for Np deposition (as also for undefined Np compounds) reaches to about 5%.

4. Conclusions

The mechanisms for the reductions of tetravalent thorium and tetravalent neptunium have been almost completely described in the solvents that we investigated.

The reduction of Th^{4+} proceeds in one step and no evidence is gained for the existence of the transient species Th(II) or Th(III). We reached the same conclusion for the reduction of $ThCl_4$ in the (Li–K)Cl eutectic [11].

Trivalent neptunium is also the transient species obtained in the reduction of Cs_2NpCl_6 in organic media as in the (Li–K)Cl melt [15].

The kinetic parameters α and k_f for both U^{4+} and Np^{4+} are very similar, at least in the solvents that we completely investigated as shown in Table 1. The k_f values are compared at the lowest overpotential in each case and only approximate values are obtained by this method; α values are computed from SP and the error 2σ is always about 0.05 except for $U^{4+/3+}$ in $DMSO_2$, where we find that $\alpha = 0.5 \pm 0.1$. These data correspond to the very similar behaviors that we observe for both actinides.

Table 1
k_f and α for HMPA, $DMSO_2$ and DMF.

Solvent	T (K)	k_f(cm s^{-1})		α	
		$U^{4+/3+}$	$Np^{4+/3+}$	$U^{4+/3+}$	$Np^{4+/3+}$
HMPA,	400	7.5×10^{-5}	1×10^{-4}	0.44	0.33
$DMSO_2$	400	2×10^{-5}	5×10^{-5}	0.5	0.40
DMF	298	1×10^{-6}	4×10^{-6}	0.24	0.35

Up to now, the only electrochemical method for preparing thorium metal and neptunium metal remains the reduction of the tetravalent species in the (Li–K)Cl eutectic as we demonstrated in previous papers [11,15]. Nevertheless, amalgamation of Np metal into a mercury-pool cathode is possible in AN with a realistic current yield, i.e. 7%. The results in AN have to be compared with similar experiments carried out with cathodic amalgamation of uranium (current yield, 21%) in oxydipropionitrile [13]. It seems that the current yield for Np amalgamation is lower than the yield for uranium; the current yield for uranium in $DMSO_2$ attained 52% [1] while a very poor yield (0.4%) has been attained in this work with neptunium. Electrodeposition of uranium metal onto solid electrodes is also easier (current yield, 18% in $DMSO_2$) [1] than the preparation of Np metal for which no result has been outlined in the present case.

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