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Electrochemical and Spectroscopic Studies of Neptunium in the Aluminum Chloride-1-*n*-Butylpyridinium Chloride Melt at 40 °C

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The chemistry of neptunium in acidic and basic AlCl₃-1-*n*-butylpyridinium chloride melts at 40 °C has been investigated by means of electrochemical and spectral techniques. In acidic as well as in basic melts, the reduction of Np(IV) to Np(III) at glassy-carbon electrodes is quasi-reversible. Indirect measurements of the formal potential and spectroscopic results on the Np(IV)-Np(III) system as a function of the acidity indicate that Np(III) and Np(IV) exist as NpCl₆³⁻ and NpCl₆²⁻ and solvated Np³⁺ and NpCl_x^{(4-x)+} (with 3 ≥ x ≥ 1), respectively, in basic and acidic melts. The apparent rate constant *k*⁰' has been measured on the basic and acidic sides. It depends on the melt acidity only in the latter melts. The Nugent linearization method has been applied to the standard potentials of Np(IV)-Np(III) and U(IV)-U(III) in 2:1 melts. A comparison with the results obtained from other room-temperature solvents shows, as already found with lanthanides, that the acidic melt is a very weak solvating medium.

Introduction

Aluminum chloride containing melts have become a class of solvents very useful for electrochemical and spectral studies of organic and inorganic solutes.¹ A proper choice of inorganic (alkali-metal)² or organic (pyridinium, imidazolium)³⁻⁶ chlorides allows one to change the working temperature of the melts from higher than 200 °C to room temperature or even lower. The acid-base properties of binary mixtures involving monochlorides have been extensively studied.¹⁻³ In particular, acidic (excess AlCl₃) melts, containing essentially large anions (AlCl₄⁻, Al₂Cl₇⁻), were shown to stabilize low cationic oxidation states⁷ as well as organic radicals.^{8,9} This interesting property has been emphasized by the recent observation of stable solutions of Tm(II),¹² which, to our knowledge, had never been obtained previously. Solutions of other divalent lanthanides (Eu, Sm, Yb) in acidic sodium⁷ and 1-*n*-butylpyridinium^{11,12} chloroaluminates, respectively, at 175 and 40 °C can also be easily prepared. A comparison of the III-II standard potentials of the lanthanides in the acidic room-temperature melt (AlCl₃-BuPyCl) with those potentials in several molecular solvents led us to conclude that the chloroaluminate melts are among the least solvating media.¹² Those earlier studies^{7,10,11} have also shown that the lower working temperature does not affect the apparent electron-transfer rate of the lanthanides couples but favors the formation of chloro complexes. As far as the actinides are concerned, a comparative study of uranium in acidic chloroaluminates (Na⁺, BuPy⁺) has been performed:^{13,14} it concluded the existence of similar chloro complexes of U(III), -(IV), and -(V), respectively, in the two melts. In that case, however, the electron-transfer rates are lower at room temperature.

The present paper reports a study of the Np(IV)-Np(III) electrode reaction at stationary and rotating glassy-carbon-disk electrodes (SGCE and RGCDE, respectively) in both basic and acidic AlCl₃-BuPyCl melts at 40 °C. When possible, the results are compared with those obtained for uranium solutions.¹⁴ The standard potentials of the two actinides, IV-III system, have been linearized according to Nugent's theory²⁹ and the results compared with those obtained from other solvents.

Experimental Section

Chemicals. The method described by Robinson and Osteryoung⁸ has been used for the synthesis and purification of 1-*n*-butylpyridinium chloride (BuPyCl), the sublimation of AlCl₃ (Fluka, "iron free"), and the preparation of the melts. Neptunium(IV) and -(III) solutions have been prepared by dissolution of Cs₂NpCl₆ and NpCl₃ obtained by classical techniques.^{15,16} Cs₂NaNpCl₆ used for comparative spectral studies has been prepared for the first time following the method described by Morss in the case of Cs₂NaNMCl₆ (M = lanthanide, Pu).¹⁷ Stoichiometric amounts of the binary anhydrous halides NpCl₃, CsCl, and NaCl have been mixed together in a quartz tube, which was then evacuated

(10⁻⁵-10⁻⁴ torr) and sealed. The mixture was heated at 850 °C for a night. The resulting product exhibits the cubic face centered (cfc) symmetry, like the Cs₂NaNMCl₆ compounds previously synthesized.¹⁷ All X-ray diffraction lines could be indexed in the cfc system. The lattice parameter, *a*, is 1.09065 ± 0.00012 nm. This value is in agreement with the results of Morss et al.,¹⁷ which indicate an increase of the lattice parameter of such compounds with the crystallographic radius of the trivalent element. Milligram scale weighings are performed with a Cahn Model gram electric microbalance.

Cells, Electrodes, and Instrumentation. All experiments have been carried out under a purified nitrogen atmosphere in a homemade Lucite box, with water content lower than 10 ppm as measured with a coulometric cell (Hygromite from Beckman). The electrochemical cell and stationary electrodes are described elsewhere.⁷ The rotating glassy-carbon-disk electrode system has been constructed in our laboratory. A glassy-carbon (GC) rod of 3-mm diameter is connected to a brass axis, and the whole system is inserted in an insulating cylinder made of Teflon. This electrode is kept in position by two ball-bearings located in a Lucite holder. The motor and the speed control unit are kept outside the box to avoid possible contamination by radioactive products. Two magnets screwed respectively to the motor and to the electrode brass axes are used for the transmission across the Lucite top wall of the box. This system provides ca. 10 discrete speed values ranging from 300 to 1500 rpm.

The potential and electrochemical measurements are made respectively with a digital Hewlett-Packard HP-3465 A voltmeter and a Princeton Applied Research polarograph, Model 170. Current-potential curves have been recorded at low scan rates (typically 2 mV s⁻¹) in order to establish quasi-steady-state conditions at the RGCDE. The positive-feedback compensation provided by the polarograph has been used to

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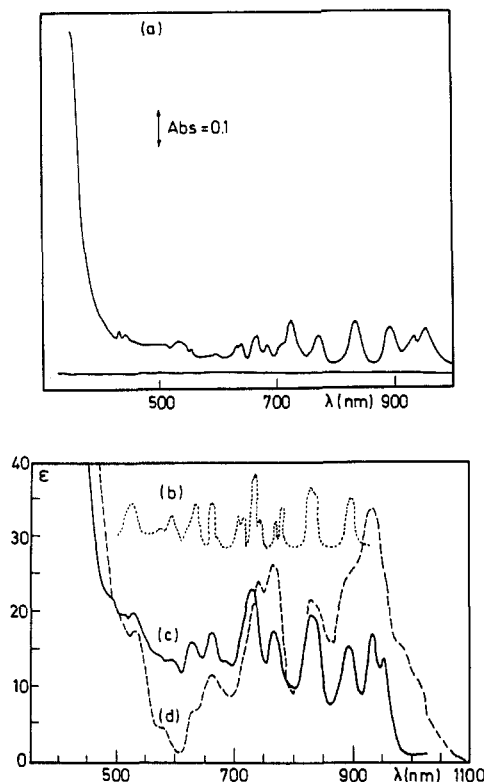


Figure 1. Molecular absorption spectra of Np(IV): (a) 1-*n*-butylpyridinium chloroaluminate (composition 49.3 mol % of AlCl_3 , $T = 40^\circ\text{C}$, $[\text{Np(IV)}] = 2.6 \times 10^{-2} \text{ mol L}^{-1}$); (b) solid Cs_2NpCl_6 ($T = 80 \text{ K}$, from ref 24); (c) pyridinium chloride ($T = 160^\circ\text{C}$, from ref 19); (d) LiCl-KCl eutectic ($T = 400^\circ\text{C}$, from ref 19).

eliminate uncompensated Ohmic drop in some linear voltammetric experiments. All potentials are referred to the potential of Al in a 57 mol % AlCl_3 melt.

Identification of the Precipitates. The precipitates formed during various experiments were filtered on glass frits and washed with dry benzene in order to eliminate traces of melt. This procedure was required in order to obtain well-defined X-ray diffraction lines. X-ray powder patterns were obtained with Kodak no-screen films, using a Philips Unit Model PW 1010.

Spectrophotometric Measurements. Raman spectra have been recorded with a modified Cary 81 spectrometer.¹⁸ Molecular absorption spectra have been obtained with 5-mm path length quartz cells and a Cary 14-H spectrometer provided with an appropriate temperature-control device. One-millimeter-thick quartz disks separated by a 0.02-mm-thick aluminum foil mask have been used for solid-state spectra. The crystals were dispersed in an optically transparent silicone oil.

Results and Discussion

As frequently observed, the results depend strongly on melt acidity and will be discussed separately for the basic and the acidic sides.

A. Neptunium Electrode Reactions in Basic AlCl_3 -BuPyCl Melts. The dissolution of the putty-colored Cs_2NpCl_6 in such melts gives a colorless solution and a white precipitate. The solid has been identified as CsCl by an X-ray powder diffraction technique. The molecular absorption spectrum of the melt is represented in Figure 1. In that figure, we have also presented spectra of Np(IV) in other chloride media where the hexachloro complex NpCl_6^{2-} is largely predominant. From the similitude observed, particularly with the solid and the pyridinium solution spectra, it can be concluded that Np(IV) is complexed as NpCl_6^{2-} in our room-temperature basic melt. The dissolution process can thus be written as



It is not very surprising to observe such a hexachloro complex for

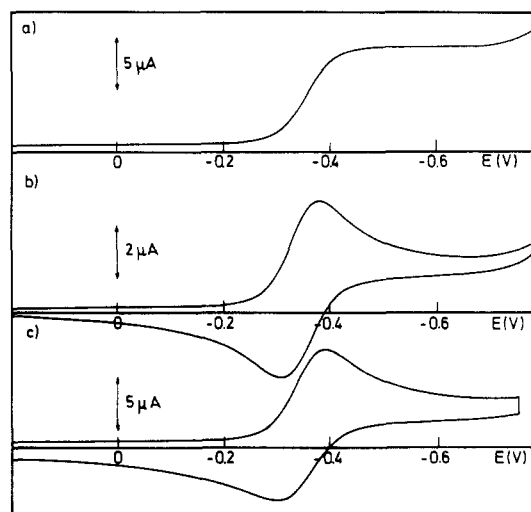


Figure 2. Reduction waves obtained on a $5 \times 10^{-3} \text{ mol L}^{-1}$ solution of Np(IV) (composition 49.3 mol % of AlCl_3): (a) voltammogram at the RGCDE (scan rate 2 mV s^{-1} , rotation speed 1000 rpm, other conditions as in (b)); (b) cyclic voltammogram (scan rate 0.01 V s^{-1} , $T = 40^\circ\text{C}$, GC electrode area 0.07 cm^2); (c) cyclic voltammogram (scan rate 0.05 V s^{-1} , other conditions as in (b)).

two reasons. First, Np(IV) is known to easily form hexacoordinated complexes in chloride media.¹⁵⁻¹⁹ Second, several studies have shown that the basic *n*-butylpyridinium chloroaluminate is a strong chloride donor solvent: for instance, FeCl_4^- , FeCl_4^{2-} ,²⁰ TiCl_6^{3-} , TiCl_6^{2-} ,²¹ EuCl_6^{3-} , and YbCl_6^{3-} ¹¹ have been identified in such melts.

Voltammograms of NpCl_6^{2-} solutions at stationary and rotating GC electrodes exhibit only one wave (cathodic) at $E^{1/2} = -0.36 \text{ V}$ (Figure 2). The peak and plateau currents increase linearly with the concentration of Np(IV). The analysis of the cyclic voltammogram wave indicates that, at 10 mV s^{-1} , the reduction is reversibly diffusion controlled with a one-electron exchange. Thus, $i_{pc}/i_{pa} = 1.01$, $|E_{pc} - E_{pa}| = 0.065 \text{ V}$, $|E_p - E_{p/2}| = 0.06 \text{ V}$, and $|E_p - E^{1/2}| = 0.03 \text{ V}$ compared to theoretically predicted values for one-electron exchange of 1, 0.062 V, 0.059 V, and 0.028 V, respectively. When the scan rate is increased, the difference between the peak potentials rises, indicating a mixed diffusion and electron-transfer rate control²² (quasi-reversible process). The analysis of the voltammograms at different rotation speeds at the RGCDE gives further information about the kinetic and thermodynamic parameters of the redox process.

For a first-order electrochemical process, with no coupled homogeneous chemical reactions, a general current-potential equation for a rotating disk electrode can be obtained from the expression of the net reaction rate of the process²³

$$v_{\text{net}} = v_f - v_b = k_f C_O(0,t) - k_b C_R(0,t) = \frac{i}{nFA} \quad (2)$$

The subscripts f and b refer to forward (reduction) and backward (oxidation) reactions, respectively, and the subscripts O and R characterize the oxidized and reduced species, respectively. The other symbols have their usual meaning. If one assumes a linear gradient of concentrations of the electroactive species

$$i = nF A m_O (C_O^* - C_O(0,t)) = -nF A m_R (C_R^* - C_R(0,t)) \quad (3)$$

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Table I. Dependence of E° , k° , α , and D_O on Melt Composition in Basic Melts at 40 °C

mol % of AlCl ₃	pCl	E° , V	$10^4 k^\circ$, cm s ⁻¹	α	$10^7 D_{\text{Np(IV)}}$, cm ² s ⁻¹	$\eta,^{20}$ g cm ⁻¹ s ⁻¹	$10^7 \eta D$, g cm s ⁻²
49.3	1.02	-0.348 ± 0.005	2.2 ± 0.1	0.7 ± 0.03	1.8	0.23	0.414
49.3	1.02	-0.353	2.4	0.71	1.9	0.23	0.437
48.3	0.65	-0.357	2.3	0.63	1.65	0.26	0.429
47.9	0.56	-0.350	1.7	0.67	1.6	0.265	0.424
46.7	0.37	-0.352	2.1	0.72	1.36	0.3	0.408
44.9	0.18	-0.348	2	0.65	1.1	0.375	0.413

and that the terms m_O and m_R are related to the rotation rate of the electrode by

$$m = 0.62D^{2/3}\nu^{1/6}\omega^{1/2} \quad (4)$$

one obtains

$$\frac{1}{i} = \frac{1}{nFA(k_f C_{O^*} - k_b C_{R^*})} \left(1 + \frac{D_O^{-2/3} k_f + D_R^{-2/3} k_b}{0.62\nu^{-1/6}\omega^{1/2}} \right) \quad (5)$$

When k_f and k_b are replaced by their usual expressions

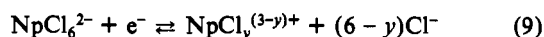
$$k_f = k^\circ \exp\left(\frac{-\alpha nF}{RT}(E - E^\circ)\right) \quad (6)$$

$$k_b = k^\circ \exp\left(\frac{(1 - \alpha)nF}{RT}(E - E^\circ)\right) \quad (7)$$

and when the oxidant is the only species in solution, eq 5 is readily transformed into

$$\frac{1}{i} = \frac{1}{nFAC_O k^\circ \exp\left[-\frac{\alpha nF}{RT}(E - E^\circ)\right]} + \left[\frac{D_O^{-2/3} + D_R^{-2/3} \exp\left[\frac{nF}{RT}(E - E^\circ)\right]}{0.62\nu^{-1/6} nFAC_O} \right] \frac{1}{\omega^{1/2}} \quad (8)$$

where all symbols have their usual meaning,²³ E° and k° being respectively the apparent standard potential and rate constant of the reaction (9).



A plot of $1/i$ vs. $1/\omega^{1/2}$ should thus be linear with a slope, $S(E)$, and an intercept, $I(E)$, both depending on the applied potential. The plots of $S(E)$ and $\ln(1/I(E))$, respectively, vs. $\exp(nFE/RT)$ and $(E - E^\circ)$ should also be linear, and the calculations, where it is assumed that $D_R \approx D_O$, yield the values of D_O , E° , α , and k° . Such a set of plots is shown in Figure 3. The linearity of the plots confirms the first order of the reduction process in the investigated concentration range (10^{-3} – 10^{-2} mol kg⁻¹).³² A similar observation has been made for the uranium system in acidic melts.¹⁴ The results of our calculations at various basic compositions are listed in Table I. The diffusion coefficients are calculated from the diffusion limiting currents and from the Levich equation.

The analysis of the results shows the following:

(1) The Stokes-Einstein relation

$$D = kT/6\pi\eta r \quad (10)$$

where k is the Boltzmann constant and r the radius of the diffusion species, appears to be obeyed across the entire acidity range investigated. The observed changes in D values are then the result of a large viscosity change rather than of a structural modification. Values of $kT/6\pi\eta D$ calculated from eq 10 lead to a radius of 5.4 ± 0.2 Å for the Np(IV) diffusing species. The satisfactory agreement with the estimated ionic radius of NpCl_6^{2-} (4.6 Å)³³ is also a confirmation of the former spectroscopic results.

(2) E° is found independent of the melt composition, which means that the number of chloride ions coordinated to the oxidized

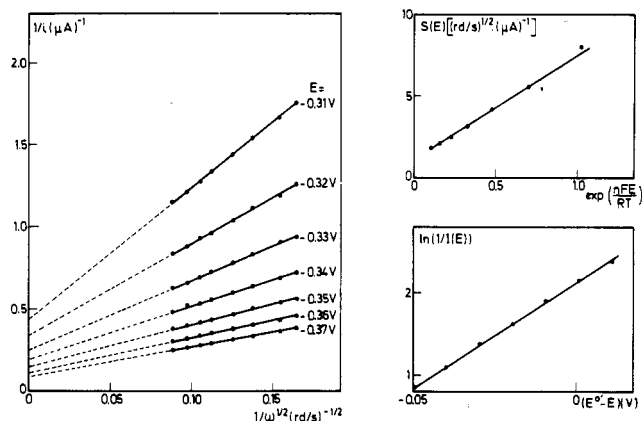


Figure 3. Plots: (a) reciprocal of the current vs. the reciprocal of the square root of the GC electrode rotation speed (composition 49.3 mol % of AlCl₃, [Np(IV)] = $5 \cdot 10^{-3}$ mol L⁻¹); (b) $S(E)$ vs. $\exp(nFE/RT)$; (c) $\ln(1/I(E))$ vs. $(E^\circ' - E)$.

and reduced species is the same. It is then interesting to note that the NpCl_6^{3-} structure has never been firmly identified even in chloride-rich solvents. In molten alkali chloride mixtures, Np(III) has a positive electrical charge lower than 3.²⁴ In highly concentrated LiCl aqueous solutions, it is coordinated to only one or two chlorides.²⁵ The existence of NpCl_6^{3-} species was postulated by analogy with heavier actinide (An) compounds of the type $\text{Cs}_2\text{NaNpCl}_6$, but $\text{Cs}_2\text{NaNpCl}_6$ has not yet been described in the literature.¹⁷ Our observations are thus denoting a stronger basicity of the basic AlCl₃-BuPyCl melt with respect to the other mentioned solvents. We also have attempted to confirm the nature of the ionic species of Np(III) by comparative spectral studies. Raman and UV-visible spectra of the newly synthesized $\text{Cs}_2\text{NaNpCl}_6$ are represented in Figure 4 together with those of basic Np(III) solutions.

The Raman spectrum of the solid shows only one weak diffusion band at 308 cm⁻¹ that could be attributed to the totally symmetrical vibration of the octahedral NpCl_6^{3-} . The intensities of the two other vibrational modes expected for the octahedral species are too weak and lie at too low frequencies²⁶ to be observed in our experimental conditions. In addition, the Raman spectrum of a highly concentrated (0.1 M) basic solution does not show significant change from that of the same pure melt. The weak 308-cm⁻¹ band could however be masked by a pyridinium cation band (Figure 4b). We have then recorded the Raman spectrum of Np(III) in a basic 1-methyl-3-ethylimidazolium chloride-AlCl₃ melt, whose chloro complexing property is probably similar and which does not present any band around 310 cm⁻¹ (Figure 4d). A weak but clearly defined polarized band appears now at 300 cm⁻¹ that can then be attributed to the NpCl_6^{3-} complex (Figure 4e).

The solid $\text{Cs}_2\text{NaNpCl}_6$ and a dilute Np(III) solution are both yellow, and their UV-visible spectra present the same general features (Figure 5). The crystal spectrum is however slightly shifted to higher wavelengths (15 nm) and exhibits a finer structure. Such differences can probably be attributed to cations

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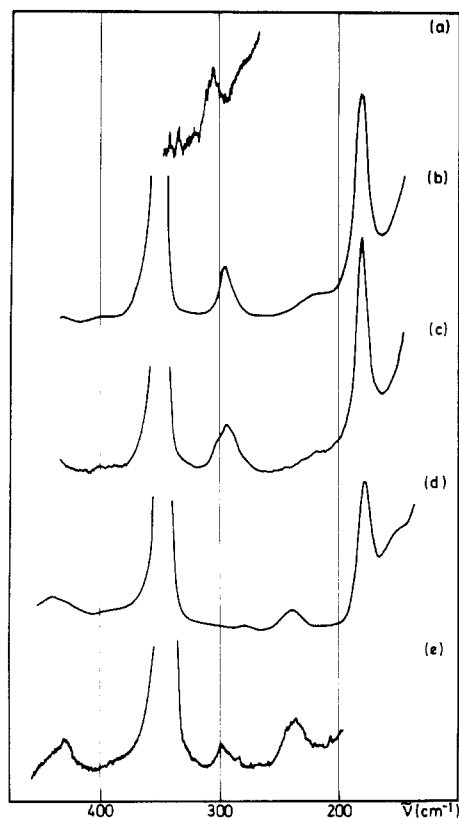


Figure 4. Raman spectra: (a) solid $\text{Cs}_2\text{NaNpCl}_6$; (b) AlCl_3 -BuPyCl melt (composition 47.7 mol % of AlCl_3 , $T = 40^\circ\text{C}$); (c) 0.1 mol L^{-1} solution of Np(III) (other conditions as in (b)); (d) AlCl_3 -1-methyl-3-ethylimidazolium chloride. (composition 47 mol % of AlCl_3 , room temperature); (e) 0.095 mol L^{-1} solution of Np(III) (other conditions as in (d)).

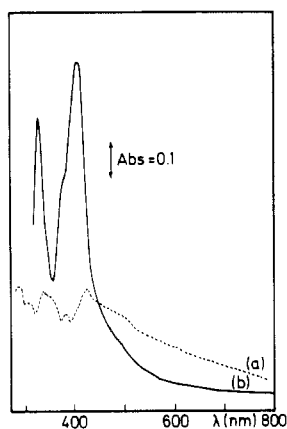


Figure 5. Molecular absorption spectra: (a) solid $\text{Cs}_2\text{NaNpCl}_6$; (b) 8×10^{-4} mol L^{-1} solution of Np(III) (composition 49 mol % of AlCl_3 , $T = 40^\circ\text{C}$)

and solvation effects³⁴ rather than to a different complexation as has been shown for the TiCl_6^{2-} complex.

The results of the two spectral studies thus support the existence of the octahedral NpCl_6^{3-} species in the basic melt.

(3) As also observed for E° , no variation of the apparent standard rate constant was measured in the investigated pCl range. k° being related to the overall oxidoreduction process between Np(IV) and Np(III) complexes, it can be affected either by a change of complexation of the oxidized or reduced species or by double-layer variations. We have shown above that the structure of the redox partners remains constant in that acidity range. Double-layer structural changes cannot be excluded, but they do not seem to affect the rate constant.

B. Behavior of Np(IV) and Np(III) in Acidic AlCl_3 -BuPyCl Melts. When a solution is made slightly acidic, NpCl_4 and NpCl_3

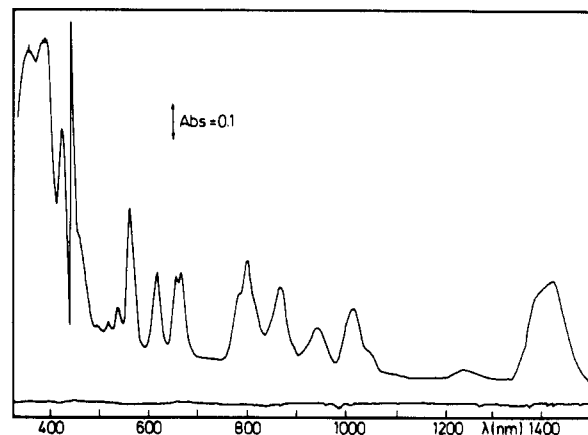


Figure 6. Molecular absorption spectrum of a 1.8×10^{-2} mol L^{-1} solution of Np(III) (composition 66.6 mol % of AlCl_3 , $T = 40^\circ\text{C}$).

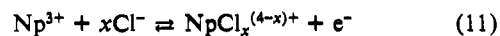
precipitate while CsCl redissolves. The precipitates redissolve when the melt is made still more acidic. Their dissolution is complete for compositions of respectively 51 and 55 mol % AlCl_3 .

B1. Neptunium(III) Solutions. The acidic Np(III) solutions are green, and their absorption spectra (Figure 6) are not modified by a composition change. The spectra of Np(III) in deuterated perchloric²⁷ and LiCl (12 M) aqueous solutions²⁵ are available from the literature. They differ only below 400 nm where the concentrated chloride solution exhibits two absorption bands with extinction coefficients 15 times higher ($\epsilon = 600 \text{ L mol}^{-1} \text{ cm}^{-1}$) than the visible bands ($\epsilon = 40 \text{ L mol}^{-1} \text{ cm}^{-1}$). Those bands have been attributed to $5f^n \rightarrow 5f^{n-1} 5d^1$ allowed transitions in the NpCl_6^{2+} and NpCl_2^+ complexes. As it can be seen from Figure 6, our spectra are similar to those of the perchloric (noncomplexing) aqueous solutions. The absorption bands below 400 nm have a low ϵ value and consequently cannot be attributed to chloro complexes. The perchloric solution spectrum is sharper than that of the melt, but the same number of bands is found in both cases. For these reasons, it is suggested that Np(III) exists as the solvated Np^{3+} cation over the whole acidic composition range. The solvation is of course different from that in perchloric solutions. This conclusion was also reached by other authors¹⁴ for U(III) in the same melt.

The oxidation of Np(III) at a GC electrode occurs just before the melt oxidation. A detailed analysis of the voltammograms obtained with the RGCDE at various rotation speeds has been performed, and the results are summarized in Figure 7. This figure shows a positive shift of E° and k° when the melt is made more acidic.

The potential shift suggests that the neptunium exhibits a different coordination in both oxidation states. The concentrations of Al_2Cl_7^- , AlCl_4^- , and Cl^- varying through that composition range, three hypotheses can be made to explain the E° changes. It has been suggested that Al_2Cl_7^- anions are involved in the coordination of Co(II) in the acidic AlCl_3 -BuPyCl melts.³⁵ Such a complexation is however unrealistic in our case. It would lead to a negative shift of E° when the melt is made acidic (increase of Al_2Cl_7^- concentration) because Np(IV) is probably coordinated to a larger number of anions than Np(III) due to its higher cationic charge density. On the other hand, an interaction with AlCl_4^- or Cl^- could describe the observed potential shift. The latter hypothesis is however more probable, simply because the precipitates that appear in slightly acidic melts are definitely binary chlorides and not tetrachloroaluminates. Finally, the same interpretation has been put forward in previous studies to explain the chemical behavior of uranium¹⁴ and lanthanides^{11,12} in such melts.

The oxidation reaction of Np(III) can thus be described by



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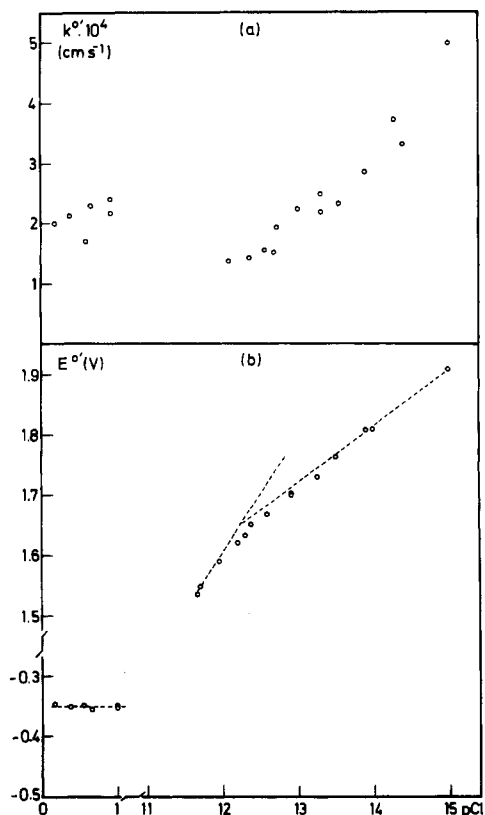


Figure 7. Plots: (a) Apparent electron-transfer rate constant of the Np(IV)-Np(III) system vs. pCl at 40 °C; (b) apparent standard potential of the Np(IV)-Np(III) system vs. pCl at 40 °C.

where Np³⁺ and NpCl_x^{(4-x)+} are solvated cationic species and for which

$$E^{\circ'} = E^{\circ} + x2.303(RT/F)pCl \quad (12)$$

The slope of the plot of $E^{\circ'}$ vs. pCl decreases from approximately 165 mV ($x = 2.7$) to 95 mV ($x = 1.5$) as the melt acidity is increased. Thus, those results suggest the existence of successive Np(IV) chloro complexes, essentially NpCl₃⁺ in the less acidic melts and NpCl₂²⁺ and NpCl²⁺ at higher pCl. The Np(IV) chloro complexes in acidic melts are thus similar to those observed for U(IV) in this room-temperature melt.¹⁴ These results reflect once again the similitude of complexation of the two neighboring actinides of identical oxidation state.

Figure 7 shows also a rough decrease of $k^{\circ'}$ when the acidity is lowered. This means that the electron-transfer rate of reaction 11 decreases when the difference of structure between the oxidized and reduced species increases. At lower acidity, the oxidation requires the formation of three Np-Cl bonds for only one at higher pCl. Such behavior has already been mentioned in water where the redox reactions $Np^{4+} \rightleftharpoons Np^{3+}$ and $NpO_2^+ \rightleftharpoons NpO_2^{2+}$ are faster than the $Np^{4+} \rightleftharpoons NpO_2^+$ one.²⁸

Finally, the values of $k^{\circ'}$ and α in a 2/1 AlCl₃-BuPyCl melt at 40 °C are of the same order of magnitude for neptunium (5×10^{-4} cm²s⁻¹ and 0.51) as for uranium (3.6×10^{-4} cm²s⁻¹ and 0.56). This is in agreement with a similar complexation of both actinide cations.

B2. Neptunium(IV) Solutions. For 54 mol % AlCl₃ mixtures, the voltammogram of Np(IV) solutions at the RGCDE shows the presence of a large quantity of trivalent neptunium (30%) that can be attributed to a spontaneous oxidation of the melt by Np(IV). The ratio [Np(III)]/Np(IV) increases with the melt acidity, Np(III) being the only stable species in mixtures containing at least 57 mol % of AlCl₃. However, it is still possible to record an oxidation voltammogram of Np(III) at the RGCDE

Table II^a

solvent	$(E - A')$, ^a V	W' , ^a V	ref	DN, ^b kJ mol ⁻¹
dimethyl sulfoxide	1.35	-3.275	c	124.7
water	1.37	-3.08	c	75.3
AlCl ₃ -BuPyCl	1.36	-1.285	d	

^a Standard oxidation potentials E° (IV-III) of actinides; values of W' and $(E - A')$; reference potential, E° of the cobaltocene-cobaltocenium system. ^b DN = donor number of the solvent, as defined by Gutmann.³¹ ^c Reference 30. ^d This work.

at those compositions. This means that the electrochemical oxidation of the melt on the GC electrode requires a large over-voltage; also the chemical oxidation of the melt should be slow because eq 8 is still obeyed.

C. Extrapolation from Nugent's Potentials Linearization Theory. Nugent has proposed²⁹ that the standard oxidation potentials $E^{\circ'}$ of the III-II and IV-III redox systems of lanthanides and actinides in the same aqueous solvent are related to q , the number of f electrons in the oxidized form, following the equation

$$E^{\circ} = W' + (E - A')q - F(q) \quad (13)$$

The values of $F(q)$, nonlinear with respect to the number of f electrons and only dependent on q (and not on the oxidation state or the chemical bonding of the ions), have been determined from atomic emission spectroscopic data on free atoms. Furthermore, we reported in previous papers^{12,30} that for several nonaqueous solvents Nugent's equation is still valid, the corrected experimental values ($E^{\circ} + F(q)$) being linearly related to q . By comparison of the various values of $(E - A')$ and W' , we pointed out for the lanthanides the following: (1) The slope $(E - A')$ is not seriously affected by the solvation of the ions, even when considering such different solvents as molecular liquids and ionic melts. (2) The intercept W' changes with the medium and reflects its solvating power. (3) The difference of solvation of the +3 oxidation state with respect to the +2 is the smallest in the acidic room-temperature melt.

From the plot of the experimental corrected potentials ($E^{\circ} + F(q)$) of U^{IV} and Np(IV)-Np(III) redox systems (at 40 °C in the 66 mol % of AlCl₃ melt) vs. q , we have calculated the $(E - A')$ and W' values. The comparison with the situation prevailing in other room-temperature solvents (Table II) leads to conclusions identical with those valid for lanthanides. The $(E - A')$ term is invariant while the W' term presents more negative values in higher solvating media and can then be related to the complexing power of solvent.

It is also possible to predict, on the basis of eq 13 that, in acidic melts, the +4 oxidation state will not be stable for actinides heavier than neptunium; also protactinium and thorium will not display the +3 state, even in this exceptionally favorable medium.

If it is assumed that all the actinide IV-III systems exhibit the same chemical behavior in basic melts (hexachloro complexes), we can also predict that both oxidation states will be stable only for plutonium and possibly uranium, in addition to neptunium.

Conclusions

(1) This work shows once more the influence of the acidity of the melt on the solute properties. The acidity affects not only the chloro complexation of the ions but also the standard rate constant of the redox process. Furthermore, the changes occur

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as well when going from basic to acidic compositions as within the acidic range itself.

(2) In acidic melts, the Np(IV)-Np(III) and U(IV)-U(III) systems exhibit similar behavior with respect to complexation and electron-transfer properties. This is in line with the fact that their ionic radii are very close to each other.

(3) The linearization method of Nugent has been applied to the actinides IV-III potentials measured in acidic melts. The comparison of our results with data in other solvents shows that the +4 oxidation state of actinides is less solvated in the melt than in other room-temperature solvents with respect to the +3 state.

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Registry No. Cs₂NpCl₆, 17030-04-5; NpCl₆²⁻, 20577-81-5; Cs₂Na-NpCl₆, 35796-99-7; NpCl₆³⁻, 58343-97-8; AlCl₃, 7446-70-0; BuPyCl, 1124-64-7; Np, 7439-99-8; C, 7440-44-0; 1-methyl-3-ethylimidazolium chloride, 65039-09-0.

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Fluoro-Containing Complexes of Chromium(III). 13. Preparation and Characterization of Some Ethylenediamine 1,3-Propanediamine Complexes¹

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The reaction of *trans*-difluorodiaqua(ethylenediamine)chromium(III) chloride, [Cr(en)F₂(OH₂)₂]Cl, with 1,3-propanediamine, tn, in refluxing absolute alcohol has been utilized to prepare *trans*-[Cr(en)(tn)F₂]Cl. Upon reaction with concentrated perchloric acid *trans*-[Cr(en)(tn)F₂]Cl yields *trans*-[Cr(en)(tn)F(OH₂)](ClO₄)₂·H₂O. The *trans*-fluoroaqua complex upon reaction with NH₄X (X = F⁻, Cl⁻, SCN⁻) in methyl alcohol yields *trans*-[Cr(en)(tn)FX]⁺. Dehydration of *trans*-[Cr(en)(tn)F(OH₂)]Cl₂·H₂O over magnesium perchlorate at room temperature produces *trans*-[Cr(en)(tn)FCl]Cl; however, there is no evidence for the formation of *trans*-[Cr(en)(tn)FBr]Br when the corresponding bromide salt is dehydrated under the same conditions. Heating of *trans*-[Cr(en)(tn)FCl]Cl or *trans*-[Cr(en)(tn)F(OH₂)]Br₂·0.5H₂O at elevated temperatures apparently produces a mixture of products, one of which is tentatively identified as *cis*-[Cr(en)(tn)FX]X (X = Cl, Br). Reaction of this mixture of products with NH₄F or NH₄SCN in methyl alcohol produces *cis*-[Cr(en)(tn)F₂]⁺ or *cis*-[Cr(en)(tn)FNCS]⁺. The geometry of *cis*-[Cr(en)(tn)F₂]⁺ was confirmed by the isolation of (-)₃₄₆-*cis*-[Cr(en)(tn)F₂]Br. By the use of optical rotatory dispersion studies (-)₃₄₆-*cis*-[Cr(en)(tn)F₂]Br was assigned the Δ absolute configuration.

Introduction

In 1973 Vaughn and Marzowski³ reported the first successful preparation of mixed-ligand complexes of the type [Cr(pn)-(aa)F₂]⁺, where pn = 1,2-propanediamine and aa = ethylenediamine (en), 1,3-propanediamine (tn), *trans*-1,2-diaminocyclohexane (dach). *Trans* isomers were easily isolated when aa = en or tn, but only the *cis* isomer was formed when aa = dach. Upon acid hydrolysis with concentrated perchloric acid the *trans*-difluoro complexes produced the corresponding *trans*-fluoroaqua cations as insoluble perchlorates. Later Seiler⁴ reported the preparation and characterization of *trans*-[Cr(pn)(en)FCl]ClO₄ as well as compounds identified as *cis*-[Cr(pn)(en)FX]X and *cis*-[Cr(pn)(tn)FX]X, (X = Br⁻, Cl⁻).

The primary objectives of the present investigation were to prepare and characterize mixed-ligand complexes of the general type [Cr(en)(tn)FX]ⁿ⁺ (X = Br⁻, Cl⁻, F⁻, NCS⁻, H₂O) and to determine what the effect of two chelate rings of different sizes would have on the preparative chemistry. In addition, it was desirable to investigate the synthetic utility of some of the *cis* isomers to prepare presently unknown mixed-ligand complexes that could be useful in kinetic, photochemical, and absolute configuration studies.

Experimental Section

Caution! Perchlorate salts of metal complexes with reducing ligands such as amines are potentially explosive, and care should be exercised when handling these materials. The explosive nature of both transition-metal perchlorates and of perchloric acid solutions of transition-metal complexes has been well documented.⁵

Ethylenediamine (en) was dried by distillation from solid potassium hydroxide pellets, and the fraction that boiled from 116 to 118 °C was collected. 1,3-Propanediamine (tn) was dried in the same fashion, and the fraction that boiled from 138 to 140 °C was collected. Methyl alcohol was dried with use of molecular sieves (4A, 4-8 mesh, Eastman Kodak) that had been previously dried.

Preparation of Starting Materials. (±)-*cis*-[Cr(en)₂F₂][Cr(en)F₄]·H₂O was prepared as previously described.⁶ *trans*-[Cr(en)F₂(OH₂)₂]Br was prepared and converted to the chloride salt by the literature method.⁷ Both the elemental analyses and electronic spectral data for the chloride salt were in agreement with the values quoted in the literature.

Preparation of *trans*-[Cr(en)(tn)F₂]Cl. A 5.0-g (23-mmol) sample of *trans*-[Cr(en)F₂(OH₂)₂]Cl was suspended in 250 mL of absolute alcohol contained in a 500-mL flask fitted with a reflux condenser. The rapidly stirred solution was heated to reflux before 4.0 mL (47 mmol) of previously dried tn was added. After 6 h at the reflux temperature the hot reaction mixture was filtered. The crude product was collected, washed with cold absolute alcohol followed by acetone, and finally air-dried; yield 4.1 g (69%). The electronic spectrum of the crude material in 0.1 M perchloric acid exhibited the multibanded pattern expected for tetragonally distorted complexes of Cr(III). Although the *trans*-[Cr(en)(tn)F₂]Cl obtained at this point is not pure, the product is suitable for further synthetic work. This reaction can be scaled up as high as 60.0 g of *trans*-[Cr(en)F₂(OH₂)₂]Cl with good results.

The filtrate from the above reaction was stored at 8 °C overnight. A second fraction (0.54 g) was collected, washed, and dried as described previously. In 0.1 M perchloric acid the electronic spectrum of the second fraction was characterized by λ_{max} 525 nm, λ_{min} 432 nm, and λ_{max} 382 nm.

Preparation of *trans*-[Cr(en)(tn)F₂]·H₂O. This complex was isolated from a 0.5-g (1.9-mmol) sample of crude *trans*-[Cr(en)(tn)F₂]Cl by the

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