THE POLAROGRAPHY OF NEPTUNIUM IN ACETATE MEDIUM

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The behaviour has been investigated of neptunium on dropping mercury electrode and on hanging mercury drop in the presence and in the absence of uranium using acetate medium.

Electrochemical techniques, *e.g.* polarography and coulometry play a very important role in the analytical chemistry of actinide elements, uranium, neptunium, and plutonium. These elements exist in a great number of valency states (the redox potentials are given in[1,2] whose stabilities are dependent on the complex formation. The results for neptunium in acetate buffer supporting electrolyte are given.

EXPERIMENTAL

The universal polarograph Radelkis OH — 105 in conjuction with a three-electrode cell assembly was used for the polarographic measurements with the dropping mercury electrode (D.M.E.), and the cyclic voltammetric measurements were carried out with an electronic potentiostat in connection with a triangular potential generator. The curves were obtained using a Kemula type of hanging mercury drop electrode (H.M.D.E).

All solutions were prepared from reagent grade chemicals. The uranium stock solution was prepared from uranium metal (NBS 960). The Np^{4+} solution was prepared electrochemically from NpO_2 (Technocommerc SU). The identification of the valency state and the formation of the acetate complex was verified spectrophotometrically.

RESULTS AND DISCUSSION

The reduction of the uranyl ions at the D.M.E. from acetate buffer supporting electrolyte shows a polarographic wave which is suitable for the determination of this element. The Ilkovič constant of maximal limiting current is high in comparison with Np^{4+} (Table I). A second wave at about $-$ 1·35 volts *vs* S.C.E. is poorly defined and hardly measureable and therefore not suitable for analytical purposes[3-5].

At high concentrations of acetate (0·2 mol/l the disproportionation of UO_2^+ is promoted, according to Harris and coworkers[6]. The authors explained similar effects by disproportionation of UO_2^+ in strongly acid medium as well as in the presence of complexing agents, *e.g.* carbonate. Two UO_2^+ molecules form one U^{4+} and

TABLE I

Ilkovič constants of maximal limiting current

Depolarisator	Medium mol/l	$\frac{\Delta E}{\Delta \log (J/J_d - J)}$ mV	$E_{1/2}$, mV	$J_d \frac{\mu A}{\text{mmol/l m}^{2/3} \text{t}^{1/6}}$	Ref.
NpIV/III	0·5 $HClO_4$	65	— 137	1·39	—
NpIV/III	0·5 CH_3COO^-	42	—1 085	1·24	—
NpIV/III + 1 . 10^{-4} mol/l UVI	0·5 CH_3COO^-	—	—1 085	1·67	—
NpIV/III + 5 . 10^{-4} mol/l UVI	0·5 CH_3COO^-	—	—1 090	1·72	—
NpIV/III + 1 . 10^{-3} mol/l UVI	0·5 CH_3COO^-	—	—1 150	6·24	—
UVI/V	0·5 CH_3COO^-	73	— 402	6·01	—
PuIV/III	0·2 CH_3COO^-	—	—	1·20	8
PuIV/III	1·0 $HClO_4$	—	—	1·47	7
NpIV/III	1·0 $HClO_4$	—	—	1·45	—
UVI/V	0·1 $HClO_4$	—	—	1·57	6

one UO_2^{2+} molecule. Electrochemically UO_2^{2+} will be reduced to UO_2^+ which disproportionates to UO_2^{2+} and U^{4+}.

Our measurements (Fig. 1*a*) with the HMDE show a well defined peak for the couple UO_2^{2+}/UO_2^+, but a hardly measureable one for the couple U^{4+}/U^{3+}.

Np^{4+} in acetate buffer medium gives an almost reversible wave with a half wave potential of $-1{\cdot}08$ volts *vs* S.C.E. The diffusion current is proportional to the concentration in the range from 10^{-3} to 10^{-4} mol/l. The same is valid for the behaviour in 0·5 M-$HClO_4$. The Ilkovič constant of maximal limiting diffusion current for Np^{4+} in 0·5 M-$HClO_4$ is in agreement with that measured by Hindman and coworkers[7]. The values for Np^{4+} and Pu^{4+} in acetate buffer solution are comparable[8]. The cyclic voltammetric curve shows well defined cathodic and anodic peaks for the couple Np^{4+}/Np^{3+} (Fig. 1*b*).

The first wave of the mixture of UO_2^{2+} and Np^{4+}, belonging to the couple UO_2^{2+}/UO_2^+ is unaffected by Np^{4+}. The second wave, belonging to the couple Np^{4+}/Np^{3+} is influenced by UO_2^{2+} as we found earlier[9]. The maximum value for the step height is reached at a concentration ratio of Np : U equal to 1 : 2 ($0{\cdot}5 \,.\, 10^{-3}$ mol/l Np^{4+} and 10^{-3} mol/l UO_2^{2+}), $I_d(Np^{4+} + UO_2^{2+}) = 4{\cdot}4 I_d(Np^{4+})$.

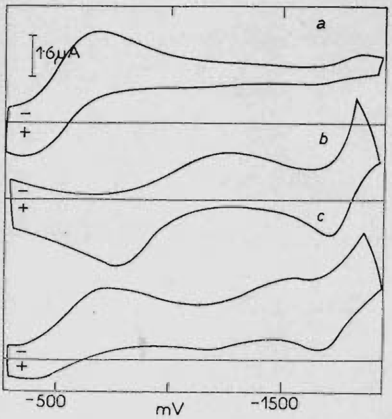

FIG. 1

Cyclic voltametric curves on HMDE. *a*: $1 \,.\, 10^{-3}$ mol/l UO_2^{2+}; *b* $5{.}12 \,.\, 10^{-4}$ mol/l Np^{4+}; *c* $1 \,.\, 10^{-3}$ mol/l UO_2^{2+}, $5{\cdot}12 \,.\, 10^{-4}$ mol/l Np^{4+}. Scan rate: 65 mV s^{-1}; $C_{ac^-} =$ = 0·5 mol/l; pH 4·6

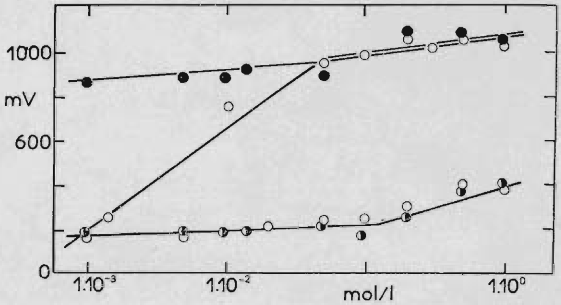

FIG. 2

The dependence of the half wave potential on the acetate concentration. ○ UO_2^{2+} or Np^{4+}; ● Np^{4+} in the mixture with UO_2^{2+}; ◑ UO_2^{2+} in the mixture with Np^{4+}. $C_{Np^{4+}} =$ $= 8{\cdot}8 \,.\, 10^{-4}$ mol/l, $C_{UO_2} = 10^{-3}$ mol/l

The cyclic voltammetric curve (Fig. 1*c*) shows a shift of the peak potential of Np^{4+} towards more negative values. The dependence of the half wave potential on the acetate concentration (Fig. 2) also demonstrates an interaction between the two depolarisators. In the mixture of UO_2^{2+} and Np^{4+} the half wave potential does not depend so much on the acetate concentration in contrast to the behaviour of Np^{4+} alone. From these results we assume the formation of a complex between Np^{4+} and UO_2^{2+} in acetate buffer medium, as it was found by Sullivan and coworkers[10] in the case of NpO_2^+ and UO_2^{2+} in perchlorate acid medium.

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