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The Polarographic Behavior of Uranium Compounds in Propanediol-1,2-carbonate and N, N-Dimethylacetamide

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The polarographic behavior of anhydrous and hydrated uranium(IV)- and uranyl compounds was investigated in propane-diol-1,2-carbonate and in N,N-dimethylacetamide. The position of the half-wave potentials (vs. aqueous saturated calomel electrode at 25°), the nature of the limiting currents, their dependency on the temperature and on the concentrations, the reversibility or irreversibility of the electrode reactions, the analytical applicability, and the influence of water are described in 0.1 M solutions of tetraethylammoniumperchlorate. Uranyl ions are reduced in a one-electron transition to U^V $UO_2^{2+} + e^- \rightarrow UO_2^+$. The half-wave potentials in different solvents are in relation to the donor number of the solvent.

Introduction

Polarographic investigations on uranium compounds in non-aqueous media were carried out in molten alkali salts,[1-6] tributylphosphate-kerosine or tributylphosphate-isopropylether,[7] anhydrous acetic acid,[8] hexane-ethanol,[9] N,N-dimethylformamide[10] and dimethylsulfoxide.[10] The polarograms of uranyl compounds show usually several waves, the first one corresponding to $U^{VI} \rightarrow U^V$.[7,9,10] Two-electron transitions $U^{VI} \rightarrow U^{IV}$ have also been claimed.[2,4,8] Investigations on anhydrous U^{IV} compounds give three waves in molten ammonium formiate,[1] two waves in N,N-dimethylformamide and in dimethylsulfoxide

$(U^{IV} \rightarrow U^{III} \rightarrow U^O)$,[10] and one wave in molten alkali chlorides $(U^{IV} \rightarrow U^{III})$.[3] In the present work uranium-(IV) and uranyl compounds have been investigated in propanediol-1,2-carbonate (PDC) and in N,N-dimethylacetamide (DMA), which are suitable for polarographic studies.[11-20]

Experimental Section

The equipment used, as well as the purification of the solvents have been described in detail.[12] Tetraethylammoniumperchlorate (TEAP) served as supporting electrolyte (0.1 M) and an aqueous saturated calomel electrode was used as reference electrode. The measurements were carrid out at $25 \pm 0.1°C$, the mercury level above the capillary end was 64 cm.

TEAP was prepared from tetraethylammoniumhydroxide and perchloric acid.[21] UCl_4 was obtained by chlorination of UO_2 with CCl_4 at 450° in CO_2-atmosphere;[22] U calcd. 62.6%, found 62.4%; Cl

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calcd. 37.4%, found 37.5%. $UO_2(ClO_4)_2 \cdot 2H_2O$ was prepared from UO_2SO_4 and $Ba(ClO_4)_2$;[23] U calcd. 47.15%, found 47.45%; Cl calcd. 14.05%, found 14.1%. $UO_2(ClO_4)_2 \cdot 2H_2O$ gave with DMA the anhydrous product $UO_2(ClO_4)_2 \cdot 5DMA$.

Anal. Calcd. for $UO_2(ClO_4)_2 \cdot 5DMA$: U, 26.35%; C, 26.55%; H, 4.98%; N, 7.75%; Cl, 7.85%. Found: U, 26.35%; C, 26.30%; H, 5.06%; N, 7.71%; Cl, 7.73%.

Anhydrous $UO_2(NO_3)_2 \cdot 1.5PDC$ was obtained by solvation of $UO_2(NO_3)_2 \cdot 6H_2O$ with PDC.

Anal. Calcd. for $UO_2(NO_3)_2 \cdot 1.5PDC$: U, 45.50%; C, 13.16%; N, 5.12%. Found: U, 45.3%, C, 13.52%; N, 5.16%.

Results

(a) *Propanediol-1,2-carbonate.* UCl_4 shows two ill-defined waves at -1.05 V and -1.37 V. The Tomeš test gives -0.098 V and -0.171 V respectively. The ratio of the wave heights is 1:3. The temperature coefficient of the sum of the both wave heights is found 1.3%/° in the temperature range from 15° to 35°. Between $c = 2 \times 10^{-4}$ and 4×10^{-3} M the Ilkovič-equation is valid. One kinetic wave ($E_{1/2} = -1.92$ V at lower concentration) is also found. Higher concentrations of UCl_4 shift the half-wave potential to -2.10 V. The temperature coefficient is 3%/°.
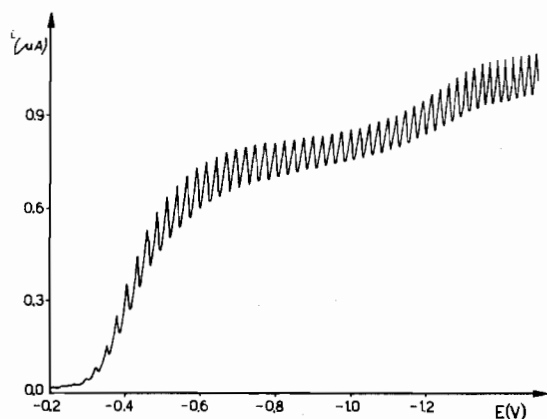

Figure 1. Polarogram of $UO_2(NO_3)_2 \cdot 1.5PDC$ ($c = 7.4 \times 10^{-4} M$) in propanediol-1,2-carbonate.

Anhydrous $UO_2(NO_3)_2 \cdot 1.5$ PDC shows two ill-defined waves at -0.41 V and -0.97 V respectively (Fig. 1). The ratio of the wave heights is 3:1. The values of the Tomeš tests (-0.134 V and -0.375 V respectively) confirm the irreversibility of the electrode processes. The temperature coefficients (between 15° and 35°) are 0.8%/° and 3.4%/° respectively. The first wave is controlled by diffusion, while the second is a kinetic wave. The wave heights increase between $c = 1.4 \times 10^{-4}$ and 1.5×10^{-3} M proportional to the concentration. With increasing concentration the half-

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wave potential of the second wave is shifted to -1.09 V. The presence of 1% water causes no essential change of the polarogram.

The hydrated $UO_2(NO_3)_2 \cdot 6H_2O$ shows a similar polarogram as the anhydrous compound. The half-wave potentials of the two waves (ratio of the wave heights 3:1) are at -0.44 V and -1.30 V. The differences between $E_{3/4}$ and $E_{1/4}$ are -0.166 V and -0.167 V and demonstrate the irreversibility of both electrode processes. The temperature coefficients are found to be 1.7%/° and 3.0%/° respectively. The limiting current of the first wave is diffusion controled, that of the second is a kinetic wave. In the range from $c = 1.4 \times 10^{-4}$ to 2×10^{-3} M the wave heigths are proportional to the concentration. The addition of 1% water causes no change of the polarogram.
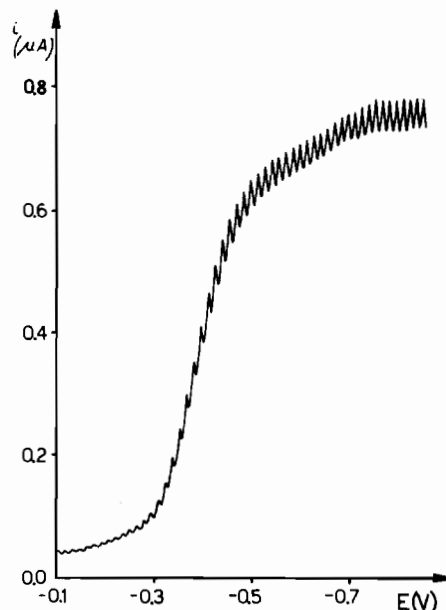

Figure 2. Polarogram of $UO_2(ClO_4)_2 \cdot 2H_2O$ ($c = 4.8 \times 10^{-4} M$) in propanediol-1,2-carbonate.

$UO_2(ClO_4)_2 \cdot 2H_2O$ shows two waves at -0.37 V and -0.55 V with a ratio of the wave heights of 3:1 (Figure 2). The logarithmic analysis of the first wave gives a straight line with a slope of -0.062 V and confirms the reversibility of the electrode process. The second wave is irreversible (Tomeš test = -0.115 V). The temperature coefficient of the more positive wave is 0.88%/°; the limiting current is diffusion controlled. In the range from $c = 1 \times 10^{-4}$ to 1.2×10^{-3} M the wave height is proportional to the concentration. At $c > 0.8 \times 10^{-3}$ M a maximum appears on the first wave; at $c = 1.2 \times 10^{-3}$ M the half-wave potential of the second wave is shifted to -1.35 V. The presence of 0.2% water does not change the polarogram. With 1% water the wave height of the first wave increases by 15% and the half-wave potential is shifted to -0.31 V.

(b) *N,N-dimethylacetamide.* UCl_4 shows three ill-defined waves at -0.65 V, -1.17 V, and -2.05 V

(Figure 3). The values of the Tomeš tests are —0.094 V, —0.147 V, and —0.163 V. The ratio of the wave heights is 2.2 : 1 : 2.9. In the range from 15° to 35° the temperature coefficient is found to be 0.81 %/° for the first wave and 1.60 %/° for the third one. The limiting currents of these waves are diffusion controlled. Between $c = 1 \times 10^{-4}$ and $1.5 \times 10^{-3} M$ the Ilkovič equation can be applied to the waves at —0.65 V and —2.05 V. At $c = 5 \times 10^{-4} M$ the polarogram changes. At a potential of —0.86 V a further small wave appears, which is increased at higher concentrations while the wave at —1.17 V is decreased. The half-wave potentials remain unchanged by addition of water, but the wave height of the first wave is increased by 0.85 % and that of the most negative wave by 30 % (with 1 % water).
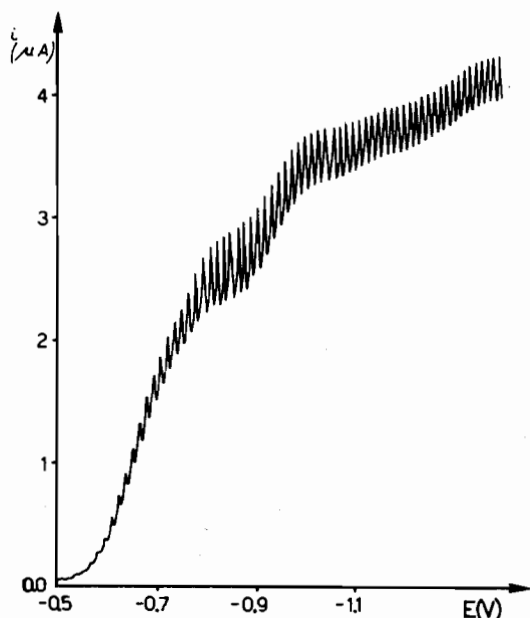

Figure 3. Polarogram of UCl₄ ($c = 1.5 \times 10^{-3} M$) in N,N-dimethylacetamide.

Anhydrous solutions of $UO_2(ClO_4)_2 . 5DMA$ in DMA show two waves (Figure 4) at —0.55 V and —1.04 V. The values of the Tomeš tests (—0.066 V and —0.267 V respectively) confirm the irreversibility of the electrode reactions. The ratio of the wave heights is 1 : 0.9. In the range from $c = 4 \times 10^{-5}$ to $6 \times 10^{-4} M$ the limiting currents are proportional to the concentration. The temperature coefficients are 0.96 %/° and 1.95 %/° respectively.

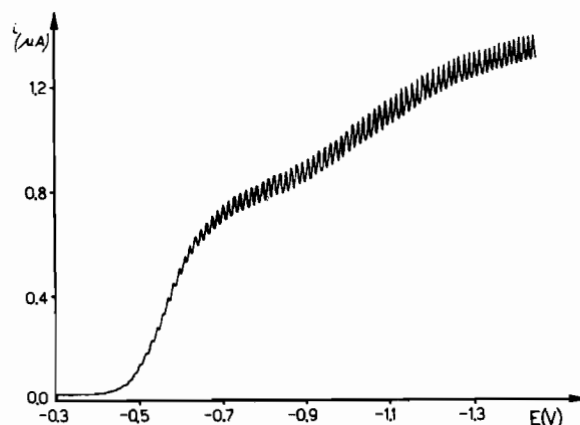Figure 4. Polarogram of $UO_2(ClO_4)_2 . 5DMA$ ($c = 4.7 \times 10^{-4} M$) in N,N-dimethylacetamide.

The polarographic behavior of $UO_2(ClO_4)_2 . 2H_2O$ in N,N-dimethylacetamide is similar to that of the anhydrous compound. At $c > 8 \times 10^{-4} M$ the more negative wave is split into two smaller waves at —0.88 V (with a maximum) and —1.44 V. At higher concentrations the wave at —1.44 V is increased and the wave at —0.88 V is decreased.

$UO_2(NO_3)_2 . 6H_2O$ shows two waves at —0.55 V and —0.97 V. Both are irreversible (Tomeš test = —0.086 V and —0.150 V respectively). The ratio of the wave heights is 2 : 1. The limiting current of the more positive wave is diffusion controlled in the range from $c = 1.5 \times 10^{-4}$ to $1.5 \times 10^{-3} M$. 1 % Water does not shift the half-wave potential of the first wave, but the wave height is increased by 10 %. At higher water content (10 %) the half-wave potential is shifted to —0.52 V and the wave height is decreased to its original value. The more negative wave forms a maximum at low water content, the wave height is decreased and at 0.5 % water the wave disappears, while at —1.55 V a new wave appears. At 10 % water the half-wave potential is shifted to —1.20 V.

Discussion

High concentration and prolonged standing of the solutions cause changes in the polarograms of uranium(IV)chloride and of uranyl compounds in both solvents. This may be explained by reaction of the

Table I. Half-wave potentials (in Volts) of $UO_2(ClO_4)_2 . 2H_2O$ vs. aqueous saturated calomel electrode and vs. the half-wave potential of Rb⁺ (italics type)

	PDC	DMF [10]	DMA	DMSO [10]
Donor number	15.1	26.6	27.8	29.8
$UO_2(ClO_4)_2 . 2H_2O$	— 0.37	— 0.44	— 0.55	— 0.53
	— 1.60	— 1.58	— 1.49	— 1.50
	— 0.55	— 0.81	— 1.05	
	— 1.42	— 1.21	— 0.99	
		— 1.36		
		— 0.66		
Rb⁺	— 1.97	— 2.02	— 2.04	— 2.03

dissolved salts with the solvent. Uranyl ions are found to be reduced, as in aqueous medium by a one electron transition to U^V:

$$UO_2^{2+} + e^- \longrightarrow UO_2^+$$
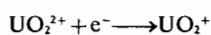
as indicated by the first wave of uranyl compounds. This has been found by logarithmic analysis (at reversible electrode processes) and by comparison of the wave heights with bisdiphenylchromium(I)-iodide. Due to the validity of the Ilkovič equation in a wide concentration range, this "uranyl wave" can be used for analytical determinations. The inter-ference of water (up to 1%) is neglegibly small. The donor number of a solvent[24,25] is a criterion of its solvating properties.[14] A relationship between the corrected half-wave potentials of an ion in different solvents and its donor number has been established.[14] The same relationship has now been found for UO_2-$(ClO_4)_2 \cdot 2H_2O$ in PDC, DMF,[10] DMA, and DMSO.[10] The underlined numbers are the values of ($E_{\frac{1}{2}Rb^+} - E_{\frac{1}{2}UO_2^{2+}}$).

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