

ELECTROCHEMICAL BEHAVIOUR OF U(VI) NITRATE IN CHLOROFORM AT A MERCURY ELECTRODE THE DEPENDENCE ON SUPPORTING ELECTROLYTE

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Abstract

The mechanistic aspects of the electrochemical reduction of U(VI) nitrate at a mercury electrode in chloroform, using three different supporting electrolytes, are described. In the presence of tetrabutylammonium perchlorate (TBAP) as a neutral electrolyte, $\text{UO}_2(\text{NO}_3)_2$ reduced in two irreversible electrochemical steps to form a U(VI)-U(V) binuclear complex and U(IV), respectively. In the presence of 0.75 M piperidinium perchlorate (PP) + 0.25 M piperidine (P) as supporting electrolyte, the reduction of $\text{UO}_2(\text{NO}_3)_2$ occurred according to a one-electron irreversible process to U(V). The same behaviour was observed in the presence of 0.5 M tributylammonium perchlorate + 0.3 M tributylamine. The diffusion coefficients of U(VI) and U(VI)-U(V) binuclear complex determined by chronoamperometric measurement are $8.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and $5.37 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ respectively.

Introduction

The electrode mechanism involved in the cathodic reduction of uranyl(VI) ion has been extensively investigated in organic solvents with high dielectric constant [1-6]. In organic solvents, the uranyl(VI) ion underwent a one electron reduction when UO_2^{2+} was not complexed in the solution. This reversible or quasi-reversible one electron transfer was followed by a chemical step whose characteristic depends on the solvent and acidity of the solution [5,6]. In contrast, when UO_2^{2+} was coordinated to ligand groups a second electron transfer was also observed which generated U(IV) in all cases [6].

S. Marouani *et al.* [7,8] have shown that the electrochemical reduction mechanism of the uranyl(VI) ion depends on the nature of the ligands. Little attention was paid to aprotic organic solvents with low dielectric

constants in which uranyl (VI) ion is present as ion-pair. The present paper deals with a mechanistic study of the electrochemical reduction of uranyl(VI) ion in chloroform ($\epsilon = 4.8$) at a mercury electrode. Furthermore, the effect of acidity of the solution and type of supporting electrolyte on the behaviour of uranyl(VI) ion was investigated. DC voltammetry, cyclic voltammetry and controlled-potential coulometry were employed as electrochemical techniques.

Experimental Section

Chemicals and Reagents

Chloroform, tri-butylamine, piperidine, perchloric acid and $\text{UO}_2(\text{NO}_3)_2$ were from E. Merck p. a. grade. The supporting electrolytes used were tetrabutylammonium perchlorate (TBAP), piperidinium perchlorate (PP)+ piperidine and tributylammonium perchlorate (tri-BAP)+ tributylamine (tri-BA). Tri-BAP was prepared by gradual neutralization of a given volume of perchloric acid 1:1 with

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the required amount of tributylamine while cooling the solution in iced water. Tri-BAP formed in slightly acid solution was filtered, then washed several times with double distilled water and dried in vacuum. The dried crystals were washed with n-hexane followed by evaporation of the solvent. The preparation of PP was as described previously [9].

Standard Uranium Solutions

A 2×10^{-2} M chloroform solution of uranyl nitrate $\text{UO}_2(\text{NO}_3)_2$ was prepared as a stock solution. The standard solutions were prepared by dilution of the stock solution.

Apparatus

All voltammograms were recorded with a three electrode system. A polarograph E 506 was used with an E 505 dropping mercury electrode (from Metrohm) to plot the DC polarograms. A multipurpose instrument from EG & G including potentiostat/galvanostat model 273, electrochemical analysis software 300 model 270 coupled with an IBM personal computer and an Epson FX 850 printer was used.

Electrodes

The reference electrode Ag/AgI (sat.), TBAI 0.05 M and TBAP 0.5 M in chloroform in a separated compartment was directly immersed in the reaction cell. The working electrodes were DME and HMDE, and the auxiliary electrode was a platinum wire.

Results and Discussion

Electrochemical Behaviour of U(VI) Nitrate in the Presence of TBAP

In the presence of 0.5 M TBAP as neutral supporting electrolyte, DC polarography of U(VI) nitrate at 10^{-3} M concentration level showed two ill-resolved reduction waves with half-wave potentials of 0.1 and -0.2 V, respectively (Fig. 1A, a); but the DP polarogram, recorded under the same conditions, exhibited two well-defined peaks (Fig. 1B). The i_1/i_2 ratio was approximately 1/3. The results of controlled-potential coulometry at the level of the first (0.04 V) and second (-0.4 V) cathodic waves reveal that these electroreduction processes need 1 mole electron per 2 and 0.5 mole of the starting U(VI) nitrate, respectively. DC polarograms recorded during the coulometry showed that the reduction products of both coulometric processes could not be oxidized at a mercury electrode under the experimental conditions, whereas the product of the first process was reducible in the potential range of the second original wave of U(VI) nitrate (Fig. 1A,b). Coulometry at the level of this wave (-0.4 V) shows that 1.5 mole electron per 1 mole of the starting U(VI) is needed.

Cyclic voltammetry of U(VI) nitrate with a scan rate of

0.02-10 V per second showed two cathodic peaks; the associated peaks on the reverse scan were not discernible. In the cyclic voltammogram obtained at the second cycle, the first reduction peak disappears (Fig. 2). This confirms that the U(VI) diffusing from the bulk was consumed in the diffusion layer by a *syn*-proportionation reaction as follows.



On the basis of the results obtained from DC polarography, controlled-potential coulometry and cyclic

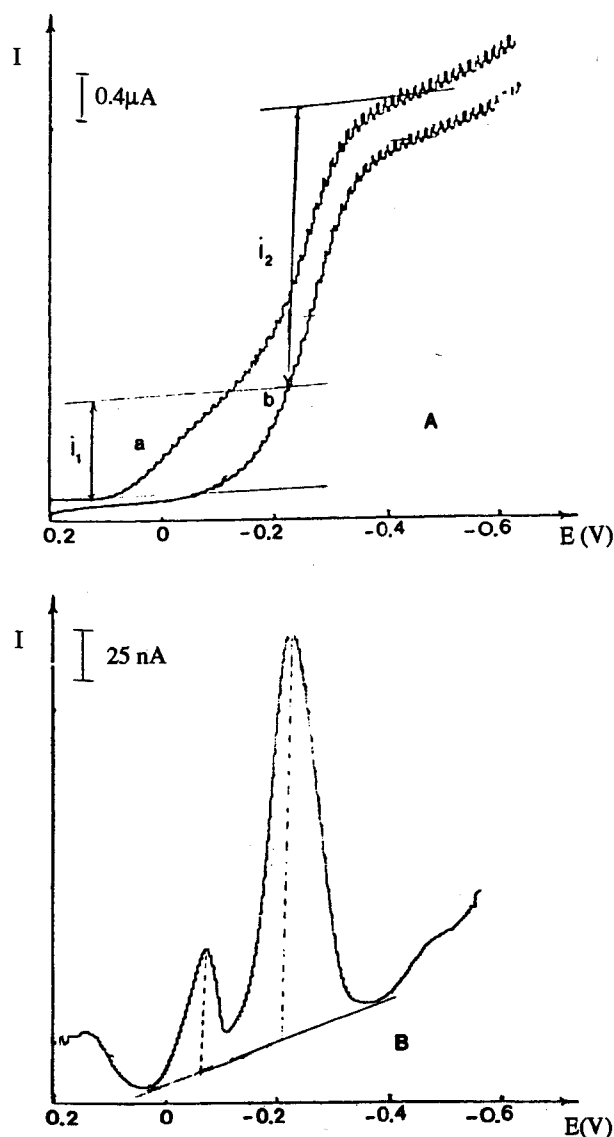


Figure 1. (A) Direct current (DC) polarograms of 0.8 mM U(VI) nitrate solution (a) before coulometry (b) after coulometry at the level of the first wave (-0.04 V). (B) Differential pulse polarogram of 10 μM U(VI) nitrate. Supporting electrolyte: 0.5 M TBAP, scan rate: 2 mV s^{-1} pulse amplitude 50 mV

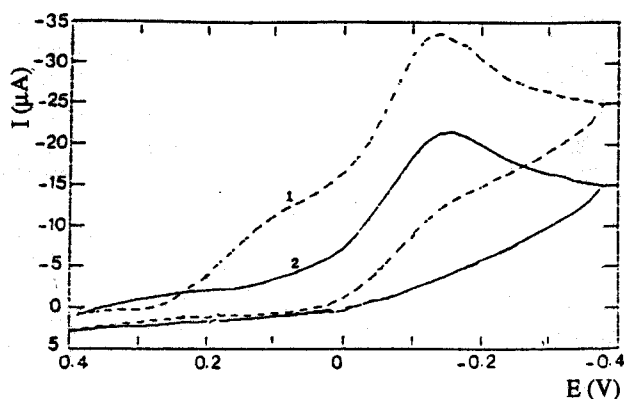
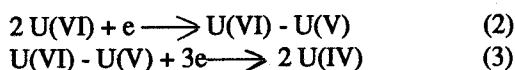


Figure 2. Cyclic voltammograms of 1mM U(VI) nitrate (1) first cycle (2) second cycle. Supporting electrolyte : 0.5 M TBAP, scan rate: 0.5 V s⁻¹

voltammetry in the presence of TBAP, the reduction steps of U(VI) nitrate may be shown as follows:



The reduction mechanism of U(VI) nitrate, proposed above, was also investigated by a DC polarographic study of the homogeneous reaction pathway which occurs between U(VI) and U(IV). This was done by gradual addition of U(VI) nitrate to the U(IV) solution generated with the aid of potentiostatically electrolysis at the level of the first reduction wave of U(VI). The polarograms recorded showed that as the concentration of U(VI) nitrate increased from zero to a value equal to three fold the U(IV) bulk concentration, only one reduction wave appeared with a half-wave potential of -0.2 V, equal to that of the second original reduction wave of U(VI) (Fig. 3, curves b-d). Note that the first original reduction wave of U(VI) appeared when the concentration of U(VI) added exceeded more than three times that of the starting U(IV) solution (Fig. 3, curve e). The results obtained from this study lead us to the conclusion that the product of reaction between U(IV) and U(VI) was U(VI) - U(V) binuclear complex, formed by a *syn*-proportionation reaction (1).

Influence of Acidity of the Medium

On the addition of 0.3 M piperidinium ion (an acid HA⁺ type) as piperidinium perchlorate to a 10⁻³ M U(VI) nitrate and 0.5 M TBAP solution, the two original cathodic waves were replaced by a single wave, with a height equal to the sum of the two original waves. The cyclic voltammograms, for all scan rates of 0.02-2 V s⁻¹, showed only one cathodic peak and the corresponding anodic peak was not discernible. The peak current was linearly dependent on the square root of the voltage scan rate (v^{1/2}) with a correlation coefficient

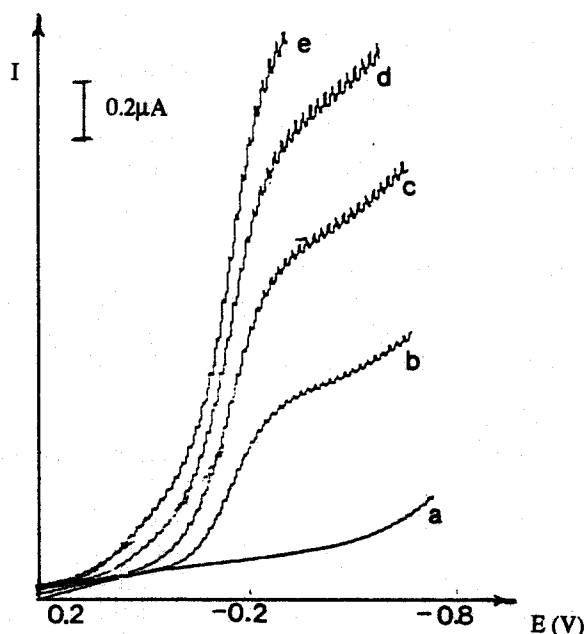


Figure 3. Direct current (DC) polarograms of (a) 0.2 M U(IV) nitrate generated with the aid of electrolysis at the level of the first reduction wave of U(VI) nitrate; (b) a + 0.2 mM of U(VI) nitrate; (c) a + 0.4 mM U(VI) nitrate; (d) a + 0.6 mM U(VI) nitrate, and (e) a + 0.8 mM U(VI) nitrate. Supporting electrolyte was 0.5 M TBAP, scan rate 2 mV s⁻¹

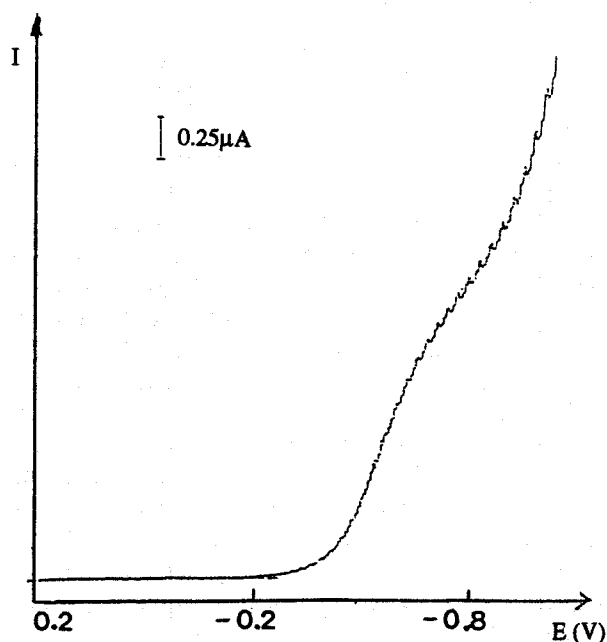


Figure 4. Direct current polarogram of 1mM U(VI) nitrate solution in the presence of 0.75 M PP + 0.25 M P as supporting electrolyte, scan rate 2 mV s⁻¹

of 0.999, confirming the diffusional nature of the current. Therefore the electrochemical reduction of U(VI) nitrate under these conditions was a two-electron irreversible process.

In the Presence of 0.75 M PP+0.25 M P

DC polarography of U(VI) nitrate with this supporting electrolyte showed one reduction wave with a half-wave potential of -0.43 V (Fig. 4). Controlled potential coulometry confirmed that the single cathodic wave obtained under these conditions corresponds to a one-electron electrochemical process. The cyclic voltammogram shown in Figure 5 indicates the reduction process is irreversible. The linearity of the peak current with square root of voltage scan rate is consistent with the diffusional nature of the cathodic current.

In the Presence of tri-BAP

The voltammograms and coulometric measurements of U(VI) nitrate in the presence of 0.5 M tri-BAP as supporting electrolyte were in agreement with a two - electron irreversible electron transfer process (Fig. 6). On the addition of 0.3 M tributylamine, conjugated base of the tributylammonium ion, to the solution, the cathodic peak disappeared completely. Apparently the U(VI) nitrate was electroinactive in this electrolyte.

Determination of Diffusion Coefficients of U(VI) and U(VI) - U(V)

The diffusion coefficients of U(VI) and U(VI) - U(V) were determined in 0.5 M TBAP in chloroform from chronoamperometric data using the Cottrell equations:

$$i = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}}$$

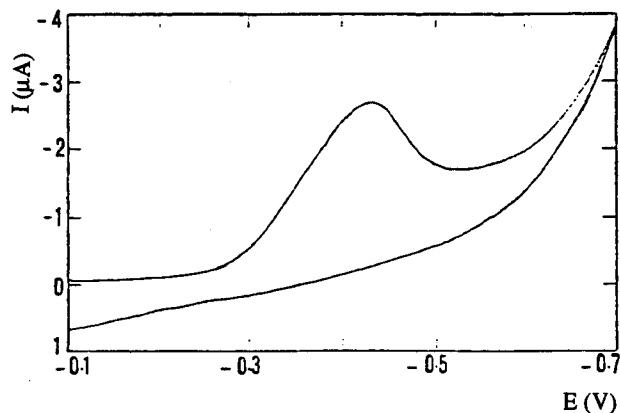


Figure 5. Cyclic voltammogram of 0.5 mM U(VI) nitrate solution in the presence of 0.75 M PP + 0.25 M P as supporting electrolyte, scan rate: 0.1 V s⁻¹

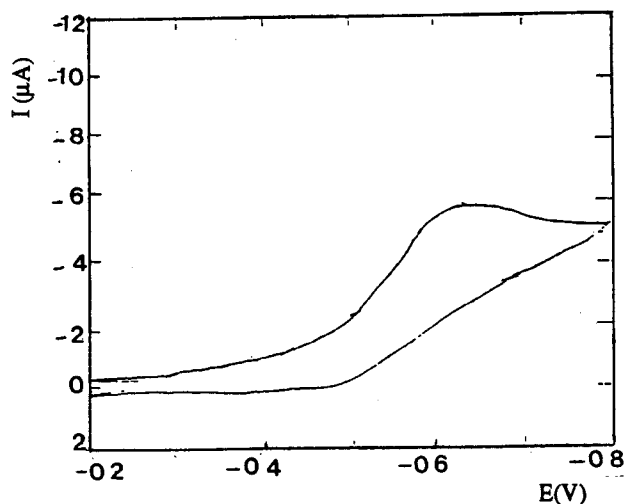


Figure 6. Cyclic voltammogram of 0.5 mM U(VI) nitrate solution in the presence of 0.5 M tri-BAP as supporting electrolyte, scan rate : 0.1V s⁻¹

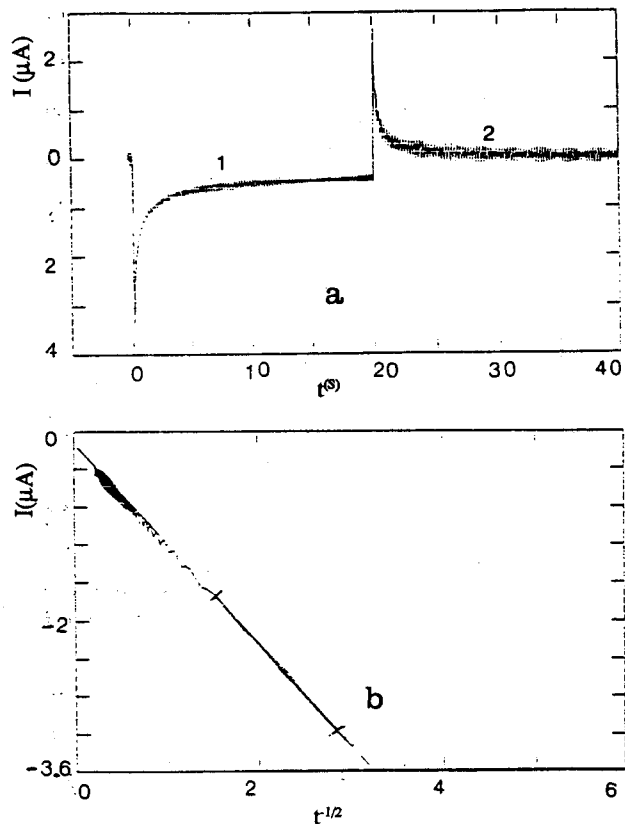


Figure 7. (a) Chronoamperogram of 0.4 mM of U(VI) nitrate on the mercury electrode (A= 0.02 cm²) at -0.4 V and 0.4 V vs the reference electrode, (b) plot of i vs t^{1/2}

where A = area of electrode (cm^2) and D_0 = diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$).

The chronoamperograms were recorded for a hanging mercury drop electrode ($A = 0.026 \text{ cm}^2$, calculated from the weight of one drop of mercury and its density) in unstirred $4 \times 10^{-4} \text{ M}$ solutions of $\text{UO}_2(\text{NO}_3)_2$ in 0.5 M TBAP. The applied potential was potential related to top of the second cathodic wave of the U(VI). An illustrative chronoamperogram is shown in Figure 7. The slope of plot of i vs $t^{-1/2}$ for the chronoamperograms is $nFAC(D/\pi)^{1/2}$ and diffusion coefficient of the U(VI) calculated is $(8.88 \pm 0.45) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. In order to determine the diffusion coefficient of U(VI) - U(V), we have prepared a $4 \times 10^{-4} \text{ M}$ solution of this binuclear complex by means of coulometry at the potential related to top of the first cathodic wave of U(VI). The diffusion coefficient, determined by chronoamperometric measurement at the potential related to the top of the cathodic wave of U(VI) - U(V) in a similar manner as described above, was $(5.37 \pm 0.66) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

Conclusion

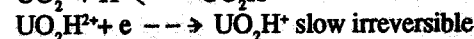
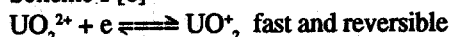
The results obtained from DC polarography, controlled potential coulometry and cyclic voltammetry revealed that the reduction of $\text{UO}_2(\text{NO}_3)_2$ in chloroform is affected by the type of supporting electrolyte. In the presence of tetrabutylammonium perchlorate as a neutral electrolyte, $\text{UO}_2(\text{NO}_3)_2$ is reduced in two irreversible electrochemical processes by forming U(VI) - U(V) binuclear complex and U(IV), respectively. On the addition of an acid (type HB^+) such as piperidinium and tributylammonium ions (as their perchlorate salts), $\text{UO}_2(\text{NO}_3)_2$ shows quite different behaviour and the two reduction waves are replaced by a single two-electron wave related to an irreversible electrochemical process.

In the presence of $0.75 \text{ M PP} + 0.25 \text{ M P}$ as another supporting electrolyte, the reduction of $\text{UO}_2(\text{NO}_3)_2$ occurs according to a one-electron irreversible process to $\text{UO}_2(\text{NO}_3)$, and U(V) formed did not reduce to U(IV). Quite similar behaviour was observed in the presence of $0.5 \text{ M tributylammonium} + 0.3 \text{ M tributylamine}$.

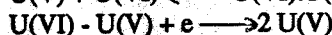
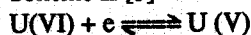
The electrochemical behaviour of $\text{UO}_2(\text{NO}_3)_2$ in chloroform in the presence of TBAP at mercury electrode may be compared with that observed in dimethylformamide (DMF), dimethylsulfoxide (DMSO), acetonitrile (AC) and propylene carbonate (PC) in the presence of tetraethylammonium perchlorate (TEAP).

For the reduction process of UO_2^{2+} in DMF, two different mechanisms were reported as the following schemes:

Scheme I [6]



Scheme II [5]



The reduction of UO_2^{2+} in acetonitrile and propylene carbonate occurred according to Scheme I. While its reduction process in DMSO proceeded according to an EC mechanism as follows [5]



As seen from this comparison, the reduction mechanism of $\text{UO}_2(\text{NO}_3)_2$ in chloroform is quite different from that obtained in DMF, DMSO, AC and PC. However, its first reduction step in chloroform and DMF is nearly similar (see Scheme II). On the other hand, $0.81 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, the value of D_0 obtained for $\text{UO}_2(\text{NO}_3)_2$ in chloroform, is close to $0.84 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ obtained in DMSO and smaller than 1.90 , 1.72 and $1.85 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ obtained in DMF, CP and AC respectively.

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