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Voltammetric Behaviour of Uranyl–Diethyldithiocarbamate Complexes in Aprotic Medium

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The polarographic investigation of the reaction between uranyl and diethyldithiocarbamate ions in DMSO evidentiates two prevailing complex species: $UO_2(DEDTC)^+$ *and* $UO_2(DEDTC)_3^-$. *The two species exhibit one reversible cathodic wave* ($E_{1/2}$ = $-0.662 V$ *and* $-1.170 V$, *respectively) both involving the reduction of the uranyl complex to uranium(V) complex. The formation of one reversible well-shaped anodic wave in the presence of diethyldithiocarbamate ion, due to the formation of mercury(II) complexes, has been already reported; in the present case, however, also the* $UO_2(DEDTC)_3^-$ *species gives an anodic wave associated with the following electrode process:*

$$2Hg^0 + UO_2(DEDTC)_3^- = 2Hg^I(DEDTC) + UO_2(DEDTC)^+ + 2e^-$$

$$2Hg^I(DEDTC) \overset{\text{rapid}}{=} Hg^{II}(DEDTC)_2 + Hg^0$$

Cyclic voltammetric tests suggest that the mentioned cathodic processes are to be considered quasi-reversible, while the anodic one, involving the ligand exchange between UO_2^{2+} *and* Hg^{2+}, *is not reversible. The stability constants of* UO_2^{2+} *and* Hg^{2+} *diethyldithiocarbamate complexes are also estimated.*

Introduction

The chemistry of uranium coordination compounds has been extensively studied and still constitutes an active field of research. A good deal of investigations has been performed by polarography and related techniques, but relatively little attention has been devoted to electrochemical studies of uranium complexes in non-aqueous media [1–15]. In this connection dimethylsulfoxide (DMSO) has been suggested [10, 16] as the most suitable aprotic solvent for polarographic investigations on dioxouranium(II) ion.

Among uranium(VI) complexing agents the polarography of dithiocarbamates, in view of their manifold uses (as pesticides, fungicides, vulcanization accelerators and anti-oxidants), has received considerable attention, mainly in aqueous [17–21] rather than in non-aqueous [22] solvents.

Furthermore the preparation of a number of uranyl–dithiocarbamates was first reported by Malatesta [23]; the coloured solutions formed by these compounds gave rise to a colorimetric method for the determination of uranium [24]. More recent investigations [25–30] dealing with the characterization of uranyl–dithiocarbamates have provided contradictory results.

The aim of the present paper is the study of uranyl–diethyldithiocarbamate complexes in DMSO. The voltammetric behaviour, the formation constants and the distribution ratio of the chelates formed between uranium(VI) and diethyldithiocarbamate are investigated.

Experimental

Chemicals

Dimethylsulfoxide (DMSO) was a "*pro analysi*" Merck product and was purified by distillation at reduced pressure [31].

$UO_2(NO_3)_2 \cdot 6H_2O$ was a reagent grade product (Merck) converted to $UO_2(NO_3)_2 \cdot 5DMSO$ by refluxing with an excess of DMSO at reduced pressure at 60 °C for 8 hours [16]; the excess of DMSO was distilled and the DMSO-solvate crystallized. The resulting yellow crystals were filtered under nitrogen, washed with benzene and dried in a vacuum oven at 50 °C.

Tetrabutylammoniumperchlorate (TBAP) was prepared from perchloric acid and tetrabutylammonium hydroxide, recrystallized from methanol and dried under vacuum.

Reagent grade sodium diethyldithiocarbamate (NaDEDTC) was used without further purification.

All other chemicals were analytical grade reagents.

Apparatus and Methods

The polarographic currents were recorded at 25 ± 0.1 °C with a three-electrode system using a Polarecord E 261 Metrohm equipped with an iR compensator, Type E 446 Metrohm. The reference electrode

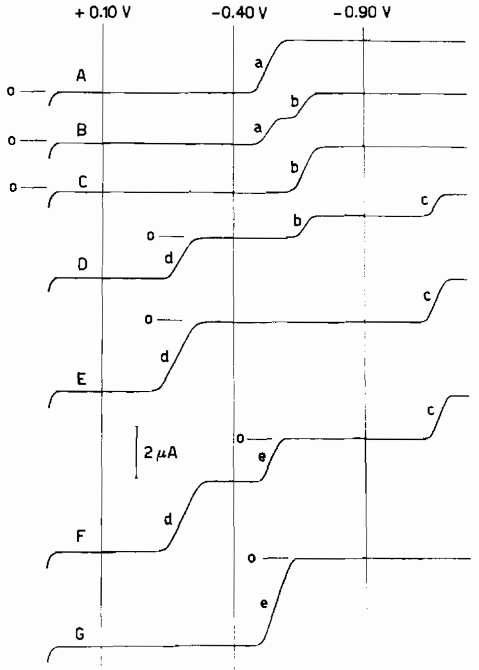

Figure 1. Polarographic profiles recorded on: 1.09 × 10^{-3} *M* UO_2^{2+} alone (A); in the presence of NaDEDTC 0.56 × 10^{-3} *M* (B), 1.14 × 10^{-3} *M* (C), 2.20 × 10^{-3} *M* (D), 3.31 × 10^{-3} *M* (E) and 4.01 × 10^{-3} *M* (F) respectively; on 1.42 × 10^{-3} *M* NaDEDTC alone (G).

was a saturated calomel electrode. The auxiliary electrode was a platinum foil of apparent area of 3 cm^2. The working electrode was a conventional dropping mercury electrode.

Cyclic voltammograms were recorded with a PAR, Mod. 170 Electrochemistry System, at a Metrohm hanging drop mercury electrode (BM 503).

Coulometric measurements were performed in a H-shaped cell with anodic and cathodic compartments separated by a sintered glass disk; the working macroelectrode was a mercury pool; the counter-electrode was a platinum foil; the reference electrode (SCE) was connected to the cell by appropriate salt bridges.

Conductometric measurements were carried out by using a LKB 3216 B bridge.

All test solutions were thoroughly degassed with DMSO-saturated nitrogen and a continuous stream of nitrogen was passed over the solutions during the measurements.

In all tests 50 ml of 0.2*M* TBAP–DMSO supporting electrolyte were used; the uranyl compound and NaDEDTC were added as weighed quantities.

Results and Discussion

Conductometric measurements have been performed at 25 °C on $UO_2(NO_3)_2 \cdot 5DMSO$ solutions in the concentration range 10^{-4}–10^{-2} *M* and, for comparison, on DMSO solutions of $NaClO_4$ and TBAP respectively at the same concentrations as the uranyl compound. The uranyl solutions gave conductance values exactly twice as great as those corresponding to $NaClO_4$ or TBAP solutions, indicating that this salt is dissociated in DMSO to the same extent as $NaClO_4$ or TBAP.

Fig. 1 outlines the polarographic curves obtained by adding increasing amounts of NaDEDTC to a uranyl nitrate solution.

The cathodic behaviour of the uranyl ion exhibited one well-defined wave with an $E_{1/2}$ of –0.53V (Fig. 1A, wave a) and a few extremely irreversible waves between –1.4V and –2.0V, probably associated with the presence of traces of water [10]. The logarithmic analysis of wave 'a' gave a straight line with a slope of 0.059V, as expected for a reversible one-electron process [10]. In the concentration range 2 × 10^{-3}–8 × 10^{-5} *M* the wave-height linearly varied both with the depolarizer concentration and the square root of the mercury height; these results confirm that the reduction process of the uranyl ion in this medium is diffusion controlled.

The addition of NaDEDTC caused the lowering of the uranium(VI) wave and the appearance of a new cathodic wave at an $E_{1/2}$ of –0.662V (Fig. 1B, wave b). The total height of the two processes was about the same as that of the wave of the uranyl ion alone.

Further additions of NaDEDTC to the uranyl solution up to a molar ratio 1/1 caused the almost complete disappearance of wave 'a', while only curve 'b' remained (Fig. 1C). The logarithmic analysis of this wave revealed a Nernstian slope of 0.065V.

Fig. 1D refers to a molar ratio $DEDTC^-/UO_2^{2+}$ of 2/1; from this profile it can be seen that wave 'b' decreases while a new cathodic process (wave c, $E_{1/2}$ = –1.17V) sets on at more negative potential values. Simultaneously an anodic process takes place, as pointed out by wave 'd' ($E_{1/2}$ = –0.18V).

At molar ratios near 3/1 (Fig. 1E) wave 'b' disappeared and only processes 'c' and 'd' were operative. The usual E *vs.* $\log[i/(i_d - i)]$ plot for wave 'c' yielded a straight line with a slope of 0.062V; the same analysis furnished a value of 0.080V for wave 'd'.

Beyond the molar ratio 3/1 a second anodic wave started out at $E_{1/2}$ = –0.545V (Fig. 1F, wave e), while waves 'c' and 'd' remained unchanged.

Further additions of NaDEDTC up to molar ratios of 6/1 caused a progressive height increment of the anodic wave 'e' and a slight shift of its half-wave potential towards more negative values.

Wave 'e' in Fig. 1G has been reported for comparison and was obtained from a DMSO solution containing the NaDEDTC ligand alone. The logarithmic analysis of this wave gave a slope of 0.060V.

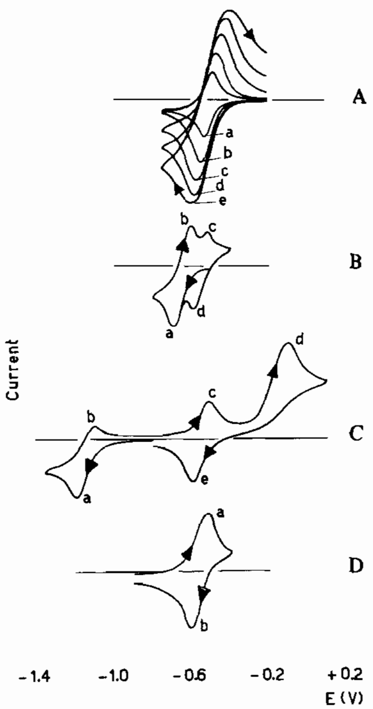

Figure 2. Cyclic voltammetric curves recorded with a mercury microelectrode. (A) UO_2^{2+} 1.0 × 10^{-3} *M* at different scan rates: 20 (a), 50 (b), 100 (c), 200 (d) and 500 (e) mVs^{-1}; (B) $DEDTC^-$ 1.1 × 10^{-3} *M* and UO_2^{2+} 1.05 × 10^{-3} *M*, scan rate: 0.1 Vs^{-1}; (C) $DEDTC^-$ 3.17 × 10^{-3} *M* and UO_2^{2+} 1.05 × 10^{-3} *M*, scan rate: 0.1 Vs^{-1}; (D) $DEDTC^-$ 5 × 10^{-4} *M*, scan rate: 0.1 Vs^{-1}.

Controlled potential coulometric experiments carried out at potential values corresponding to the limiting current of wave 'a', Fig. 1A (–0.80V), gave a n_e mean value of 1.2. Polarograms recorded just at the end of the electrolyses gave a cathanodic wave with $E_{i=0}$ very near to the $E_{1/2}$ for the uranyl ion reduction; the anodic branch was notably higher than the cathodic one. As already reported [16] this behaviour had to be expected for the U(VI)/U(V) system in DMSO, owing to the slow reoxidation of the electrogenerated U(V) species; this accounts for the obtained value of n_e higher than one.

Coulometric tests performed at –0.90V on solutions containing NaDEDTC and uranyl nitrate in the molar ratio 1/1 gave again a n_e value slightly higher than one (n_e = 1,1). A similar result (n_e = 1.3) has been also obtained at –1.30V for solutions containing the cited species in the molar ratio 3/1. In our opinion also these results, which are higher than the theoretical value of one, are to be attributed to the chemical reactions involving the U(V) species [16].

On the basis of the obtained coulometric data, the cathodic processes relative to curves 'a', 'b' and 'c' in Fig. 1 can be considered reversible.

Controlled potential coulometric tests performed on wave 'd', Fig. 1E (+0.15V), indicated that one mol of electrons per mol of NaDEDTC was consumed. The polarograms recorded on the electrolyzed solution showed that no anodic wave was still present, while the cathodic picture resulted rather complicated; in fact a wave with $E_{1/2}$ at –0.52V appeared, immediately followed by a large maximum which extended for about 0.2V precluding any accurate evaluation of successive waves; the same complicated polarographic picture was obtained by adding $Hg(NO_3)_2$ to a DMSO solution containing UO_2^{2+} and $DEDTC^-$ ions in the ratio 1/2. The logarithmic analysis of wave 'd' and the coulometric results suggest that the charge transfer process is now characterized by an appreciable overvoltage.

The polarographic and coulometric results obtained by studying the electrode process occurring at wave 'e' (Fig. 1G), relative to the NaDEDTC alone, well agreed with previous data in acetone medium [22], indicating a one-electron reversible polarographic process.

To gain further information about the above polarographic processes some cyclic voltammetric measurements have been carried out.

The tests performed on uranyl solutions (Fig. 2A) indicated that the electrode process, which could be considered polarographically reversible, was indeed more complicated. In fact a noticeable shift of the E_p value with the scan rate has been observed and the current function ($i_p/v^{1/2}$ *vs.* v) decreased with increasing scan rate; in addition the potential difference between cathodic and associated anodic peaks ($E_p^c - E_p^a$) increased from the theoretical value of 59 mV at low scan rate (10–20 mVs^{-1}) up to very high values (about 400 mV) at scan rates of the order of 1Vs^{-1}, while the ratio between anodic and cathodic peak-currents (i_p^a/i_p^c) was substantially very near to one. The obtained $E_{1/2}$ value for the uranyl ion reduction resulted in good agreement with previous data [10, 11]; it has been also confirmed that the interference of water is negligibly small, but the qualitative cyclic voltammetric tests suggest that the uranyl reduction cannot be considered completely reversible in DMSO medium.

Fig. 2B shows a typical cyclic voltammetric curve relative to a solution containing NaDEDTC and UO_2^{2+} in the molar ratio 1/1. By scanning in the cathodic direction, from a starting potential of –0.500V, peak 'a' (E_p = –0.70V) can be observed, with an associated anodic peak 'b' (E_p = –0.62V) in the reverse scan. A small anodic peak ('c'), located at –0.53V, also appeared associated in its turn to the cathodic peak 'd' (E_p = –0.60V). The ΔE_p value between the peaks 'a' and 'b' and the current ratio (i_p^a/i_p^c) suggest that the involved process can be considered quasi-reversible. The E_p value of peak 'a' corresponds to the process of curve 'b', Fig. 1, just as the anodic peak 'c' has to be related to curve 'e' in the same figure.

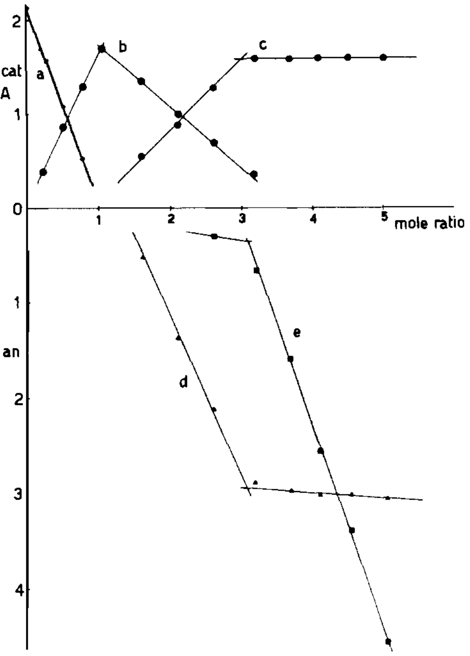

Figure 3. Current trend of the polarographic processes as a function of the mol ratio DEDTC$^-$/UO$_2^{2+}$. (·) uranyl ion reduction; (o) reduction of the first complex species; (●) reduction of the second complex species; (▲) first anodic process; (■) second anodic process.

In Fig. 2C a cyclic voltammogram recorded on a solution containng NaDEDTC and UO$_2^{2+}$ in the molar ratio 3/1 is reported. By scanning from a starting potential of −0.80V a sharp cathodic peak ('a') located at −1.20V appeared; in the reverse scan a small associated peak ('b') could be observed (E_p = −1.10V) only at scan rates higher than 0.1Vs^{-1}, indicating that the electrode process is not quite reversible, but should be complicated by reactions following the charge-transfer step. Peak 'a' just occurs near the $E_{1/2}$ value of curve 'c', Fig. 1. The anodic peak 'd', which appears at −0.10V either after traversing peak 'a' or by scanning directly in the anodic direction is to be related to wave 'd', Fig. 1; the absence of any associated peak confirms the irreversibility of this process as suggested also by the polarographic data.

The cyclic tests performed on NaDEDTC solutions gave the voltammetric picture reported in Fig. 2D. Starting from −0.90V and scanning towards positive potentials a sharp anodic peak appeared (E_p = −0.53 V) with an associated cathodic one (E_p = −0.60V). The ΔE_p value and the current ratio (i_p^a/i_p^c) agree with the polarographic data, supporting the reversibility of the process. Hence peaks 'c' and 'd' in Fig. 2B together with peaks 'c' and 'e' in Fig. 2C have to be attributed to the DEDTC$^-$ species.

In Fig. 3 the current trend of the observed polarographic processes against the mol ratio (DEDTC$^-$/UO$_2^{2+}$) is plotted; the symbols a, b, c, d, e refer to the corresponding waves of Fig.1. At first there can be noted the almost complete formation of the 1:1 complex, as demonstrated by the progressive decrease of the uranyl reduction current (a) while the cathodic current of the 1:1 complex (b) increases, reaches its highest value just at the mol ratio 1/1, then gradually decreases to the ratio 3/1. As soon as the 1:1 complex decreases a second complex species (c) appears and in turn reaches the maximum current value at the ratio 3/1. These results point out that in DMSO the prevailing UO$_2^{2+}$–DEDTC$^-$ complexes should be UO$_2$(DEDTC)$^+$ and UO$_2$(DEDTC)$_3^-$.

Since the present electrode processes correspond to a reduction of complexes to a lower oxidation state and since no shift in half-wave potential was observed for each of the two complexes, unfortunately only the ratio of the stability constants of the oxidized and reduced forms can be computed [32]. By using the equation:

$$\Delta E_{1/2} = \frac{RT}{F}\ln\frac{K_{U(VI)complex}}{K_{U(V)complex}}$$

the following ratios of constants were obtained:

$$\frac{K_{1\,U(VI)complex}}{K_{1\,U(V)complex}} = 1.6 \times 10^2;$$

$$\frac{K_{3\,U(VI)complex}}{K_{3\,U(V)complex}} = 5 \times 10^{10}$$

where K_1 and K_3 refer to the 1:1 and 3:1 complexes respectively. As expected the stability constants values confirm that the uranium(VI) species is more strongly coordinated to the ligand than the uranium(V) one. Until now few data on uranium complexes in nonaqueous media are available, preventing an accurate comparison of stability constants; in this connection, however, it can be noted that the polarographic behaviour and the stability constant ratios obtained for uranyl–acetylacetonate [12] are similar to those reported above.

It is interesting to note that the UO$_2$(DEDTC)$^+$ complex was never surely evidentiated, while UO$_2$(DEDTC)$_3^-$ was already reported [29, 30]. Our results do not indicate the formation of the 2:1 complex, previously described in aqueous medium [23]; however this could be due to a lower formation constant in comparison to those of the 1:1 and 3:1 complexes or to an unusual similarity between the stability constant values for the 2:1 complex of uranium(VI) and uranium(V).

The anodic current 'e' of Fig. 3, which starts near the ratio 3/1, involves the formation of a mercury(II)–DEDTC$^-$ complex in agreement with previous reports [19, 21, 22], according to the EC scheme:

$$DEDTC^- + Hg^0 = Hg^I(DEDTC) + e^-$$

$$2Hg^I(DEDTC) \overset{rapid}{=} Hg^{II}(DEDTC)_2 + Hg^0$$

The linear increment of this anodic current suggests that no successive strong complexes are formed between UO_2^{2+} and $DEDTC^-$ ions at molar ratios higher than 3/1 under the experimental conditions. The mentioned polarographic reversibility of the process allows us [33] to calculate an approximate mean value for the formation constant of the complex $Hg(DEDTC)_2$; this value results very high, $pK = -42.3$ (of the same order of magnitude as the mercury(II) tetracyanide complex in aqueous media [34]).

An interesting feature of the present investigation is implied in the anodic curve 'd' of Fig. 3, which starts just beyond the ratio 1/1 and reaches a maximum at a $DEDTC^-/UO_2^{2+}$ ratio of 3/1. This anodic process cannot be attributed to the direct $DEDTC^-$ oxidation, which occurs beyond the mercury discharge [22]. Indeed this electrode process involves again the formation of the mercury(II)–$DEDTC^-$ complex, but in this case the $DEDTC^-$ ion must be supplied by the $UO_2(DEDTC)_3^-$ species formed in solution; this constitutes a ligand exchange process. The high value of the stability constant for the mercury(II) complex justifies this exchange, but it requires more positive potential values than those in the presence of free $DEDTC^-$ ion. By analogy with the previous anodic process this one also can be described in terms of the following EC mechanism:

$$2Hg^0 + UO_2(DEDTC)_3^- = 2Hg^I(DEDTC) + UO_2(DEDTC)^+ + 2e^-$$

$$2Hg^I(DEDTC) \overset{rapid}{=} Hg^{II}(DEDTC)_2 + Hg^0$$

The occurrence of this exchange process has been checked by adding an amount of $Hg(NO_3)_2$, equivalent to the uranyl content, to a solution containing UO_2^{2+} and $DEDTC^-$ ions in the ratio 1/2; the orange–yellow colour of the solution vanished, while the polarographic picture clearly indicated the disappearance of wave 'c', the formation of a large maximum due to the reduction of the mercury(II) complex ($Ep \cong -0.6V$) and the partial reappearance of wave 'a'. Also the coulometric data (one mol of electrons per mol of $DEDTC^-$ ion) support the above suggested mechanism. In addition the presence of this anodic wave (wave d, Fig. 3) just beyond the 1/1 ratio suggests that the $UO_2(DEDTC)^+$ complex is stable enough to prevent the formation of the mercury(II) complex, which forms on the contrary in the presence of the $UO_2(DEDTC)_3^-$ species. Moreover the sizable $\Delta E_{1/2}$ value between wave 'e' and 'd' (about 0.4V) confirms that the cited exchange reaction is surely quantitative.

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