Influence of Solvents on Electrochemical Reduction of Uranyl Complexes

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Abstract: The electrochemical reduction of uranyl salicyladehyd acetyl hydrazone complex was studied on mercury electrodes in DMSO, DMF and PC (Propylene Carbonate) as solvents, by voltammetric techniques and dc polarography, The behaviour of the complex are different in each solvent and depend of Gutmann's donor number. The mechanistic aspects invoved have been studied.

Key words: Solvent, electrochemical, reduction, DMSO, DMF, PC

INTRODUCTION

Redox properties of uranyl in aqueous solutions containing non-complexing subtances have been studied by many investigators (Zanello, 1977; Hiroshi *et al.*, 1986; Chie *et al.*, 1993; Dueber *et al.*, 1994; Pournaghi *et al.*, 1997). In such media, we can have 2 or 3 steps which depend on the pH and the nature of the supporting electrolyte. The general conclusion of the study of the electrode reaction corresponding to the first polarographic wave (at potential approx.-0.2 V/SCE) is that the one electron reduction of uranyl ion (UO_2^{2+}) results in the formation of UO_2^+. The reversible nature of this reaction was recognised by the majority of the authors. The second polarographic wave (at approx.-0.8 V/SCE) corresponds to the irrevesible reduction of U(V) to U(IV). In complexing media (Tsai and Wei, 1974; Issa *et al.*, 1975; Chyan and Laie, 1976; Zanello *et al.*, 1977; Sindhu *et al.*, 1982; Marouani *et al.*, 1988) the effect of ligands substitution on electrochemical reduction of uranyl ions investigated. The stability constants of the complexes species were determined also kinetics parameters. An electrode reaction mecanisms of reducion was proposed.

In non-aqueous media, the cathodic reduction of uranyl (VI) has received little attention (Louati *et al.*, 1991; Zanello *et al.*, 1986; Palys *et al.*, 1993; Lee *et al.*, 1996; Muziguchi *et al.*, 1998; Kim *et al.*, 2002; Misioka *et al.*, 2003). The properties of reduction products have not been examined in detail. A systematic study (Zanello *et al.*, 1982) shows that the physico-chemical properties of solvents influence the redox behaviour of UO_2^{2+} another study (Marouani *et al.*, 1987) mentioned that the reduction of UO_2^{2+} ion is a reversible transfer followed by a chemical step. Its characteristics depended on the solvents. In this connection the present study deals with mechanistics of electrochemical reduction of uranyl (VI) salicylaldehyd acetyl hydrazone complex in some non-aqueous solvents. As a further aim we intend to investigate the solvation process of UO_2^{2+} complex in the various solvents.

MATERIALS AND METHODS

The polarographic and the cyclic voltammetry curves recorded using a unit of measure PRG4-GSTP3(Solea-Tacussel). This apparatus allows us to achieve pulse polarographic measurements and cyclic voltammetry. Coulometric measurements were performed on mercury-pool electrode (area 6 cm^2) with above unit associated with an electronic integrator IG-6N (Tacussel). The reference electrode was calomel electrode in a saturated aqueous solution of KCI (SCE) electrically connected to the studied solution by a junction bridge filled with the studied solution without electroactive species.

Electrochemical measurements were carried out under argon at controlled temperatures (25°C) on dropping mercury electrodes.

The solvent considered, Dimethyl Sulfoxide (DMSO), Dimethyl Formamide (DMF) and Propylene Cabonate (PC) were reagent grade products, further purified according to established procedures (Mann, 1968).

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Fig. 2: Reverse normal-pulse polarogram of the complex in DMSO [drop time 2 sec, delay 1.90, pulse duration 40 ms]
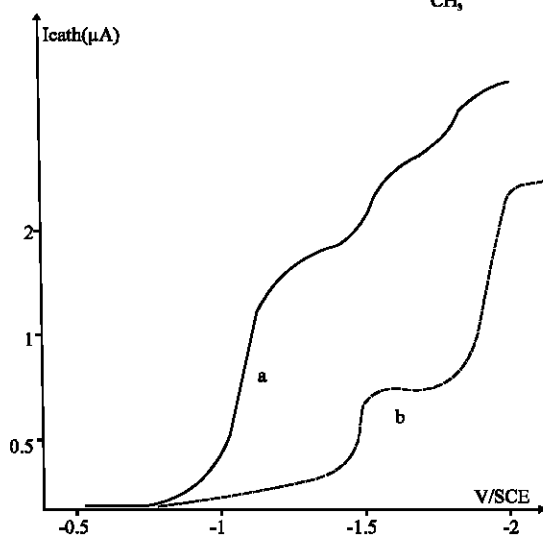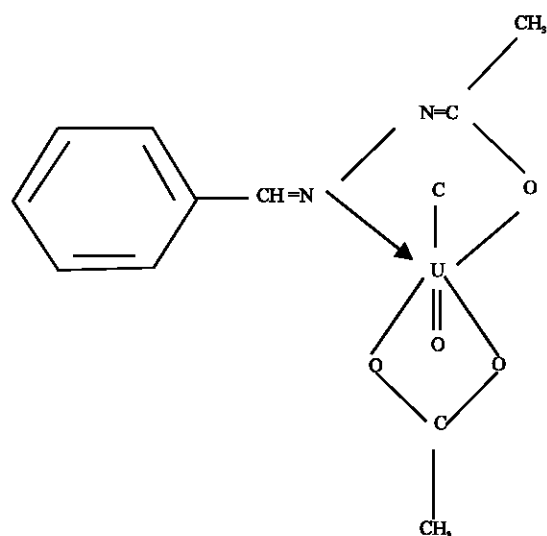

Fig. 1: DC polarogram of the complex in DMSO/0.1 M TBAP, Ligand reduction in DMSO

Tetra-n-Butyl Ammonium Perchlorate (TBAP) as background electrolyte was purified by dissolution in a small volume of methanol, then precipitated in a large volume of distilled water and finally dried at least 48h at 60° under reduced pressure.

The complex of uranyl with salicyl aldehyd acetyl hydrazone was perpared according to known procedures (Yacouta and Mustapha, 1990) and the suggested structure is as follows: (We notice the presence of one acetate molecule).

RESULTS AND DISCUSSION

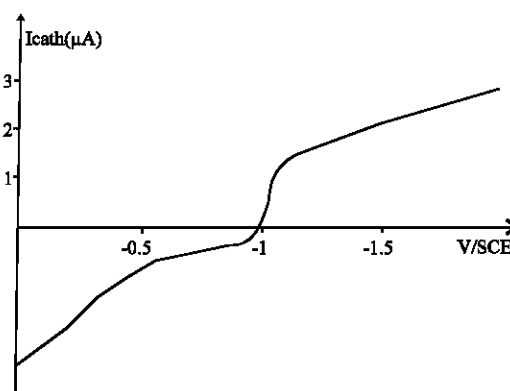**Dimethyl Sulfoxide (DMSO):** The study of DMSO, TBAP 0.1 M, solution of the complex by dc polarography at controlled drop time (Fig. 1a) shows three well defied reduction waves at -1.14, -1.58 and -1.80 V/SCE, However, the reduction of the ligand in the same conditions (Fig. 1b) gives only 2 waves at -1.6 and -1.80 V/SCE, by comparison with waves complex we can attribute te two last waves of reduction of the complex to the reduction of the ectrogenerated ligand. We focus our study only for the first wave.

In order to determine the nature of the limiting current, the dependence of the wave high on concentration and mercury colon high was checked. The limiting current is controlled by diffusion in concentration range from $1,2.10^{-4}$ to 2.10^{-3} M.

Logarithmic analysis of the first wave results in a straight line with a slope of 0.080 indicates the quasi-reversible one electron transfer.

As already observed in dc polarography, normal pulse polarography from 0 to -2 V/SCE, exhibits three reduction waves. Moreover, Reversed Pulse Polarograms (RPP) (i.e., Scanning towards anodic potentials) from -1.5 to 0V/SCE (Fig. 2) reveal that only the first wave has a reversible character.

The number of electron taking part in the electrode process of the first step is one. The analysis of the coulometric curves $\log I/I_0 = f(t)$ indicates that the first transfer of electron is followed by a chemical reaction. The plot $\log I / I_0 = f(t)$ is not linear.

A typical votammogram is given in Fig. 3. In the potential range 0 to -1.4 V/SCE we observe one cathodic peak to which an anodic peak is directly associated in the reverse scan. Tests performed at potential scan rates, v, ranging from 2 to 100 $V.S^{-1}$ showed that: the potential peak, as difference between the half peak potential value, $E^c_p /2- E^c_{p,}$ shift towards negative value as v increases, the
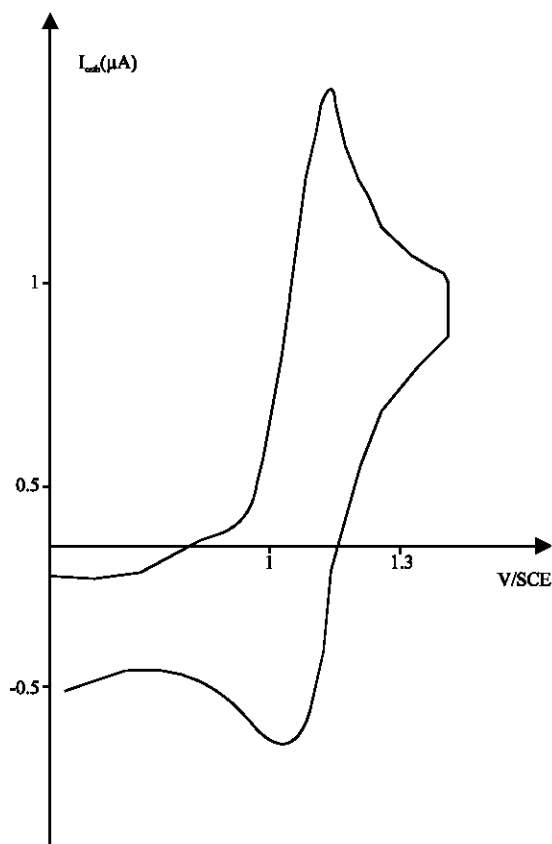
Fig. 3: Cyclic voltammetry of the complex (3. 10-3 M) in DMSO [v = 5 V.s-1, scan between 0 and -1.4 V/SCE, electrode Hg]
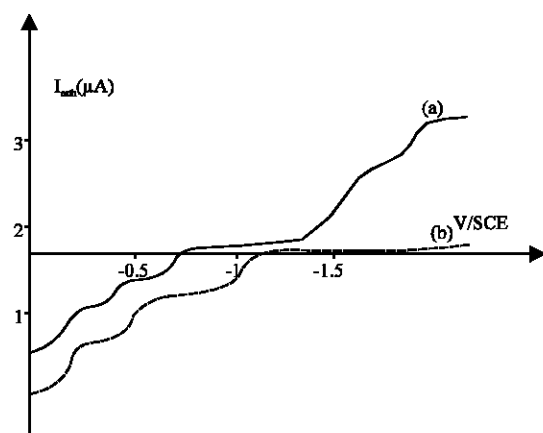

Fig. 4: Dc polarogramm in DMSO / 0.1 TBAP
    (a) after total reduction of the complex at -1.2 V/SCE
    (b) After total reduction of ligand at -1.9 V/SCE

difference between the peak potential value of the reoxydation peak and that reduction $E^a_p - E^c_p$; progressively increases with v.

The current peak value of the cathodic peak, I^c_p increases with v and the plot $I^c_p = f(v^{1/2})$ is not linear. The
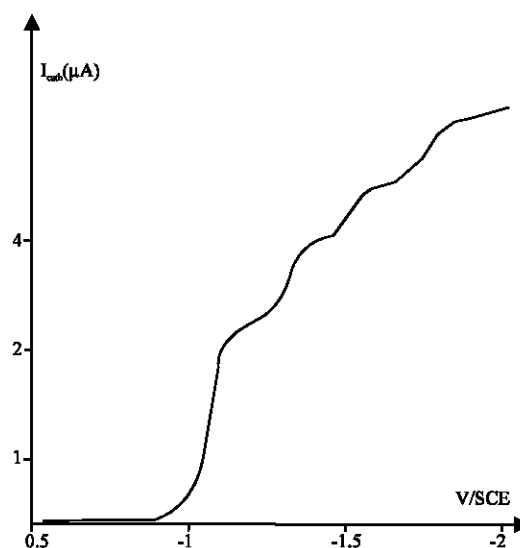

Fig. 5: Polarogram of the complex in DMF/0.1M TBAP

anodic to cathodic current peak ratio I^a_p / I^c_p is constant and less than one.

All this data are consistent with a quasi-reversible charge transfer followed by a chemical reaction that destroys the electrogenerated species (Nicholson and Shain, 1964).

The complete reduction of the complex at -1.2 V/SCE shows in polarography three new anodic waves at -0.7; -0.4 and -0.1 V/SCE and the absence of the first step of reduction.

The polarogam of the ligand solution totally reduced at -1.9 V/SCE shows three anodic waves at - 1.0; - 0.4 and - 0.1 V/SCE (Fig. 4)

On the basis of these results, obtained from dc polarography, voltammetry and controlled potential coulometry, we can say that the reduction of salicyl aldehyd acetyl hydrazone of uranyl in DMSO could be tentatively formulated as follows:

Scheme 1:

E   [U(VI)O₂L.Ac] +e   ⇄   [U(V)O₂L.Ac]⁻

C   [U(V)O₂L.Ac]⁻   →   [U(V)O₂L.Ac] +L⁻
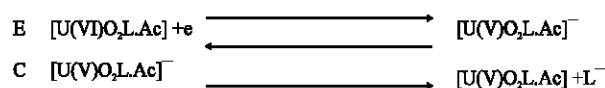
Dimethylformamide (DMF): In Fig. 5 the polarogram of uranyl (VI) complex in DMF, TBAP (0.1M) consist of four waves with a half-wave potential of -1.03; -1.35; -1.6 and -1.8 V/SCE, By comparison with the cathodic behaviour of the corresponding free ligand, the 2 last waves have to be attributed to ligand charge transfer.

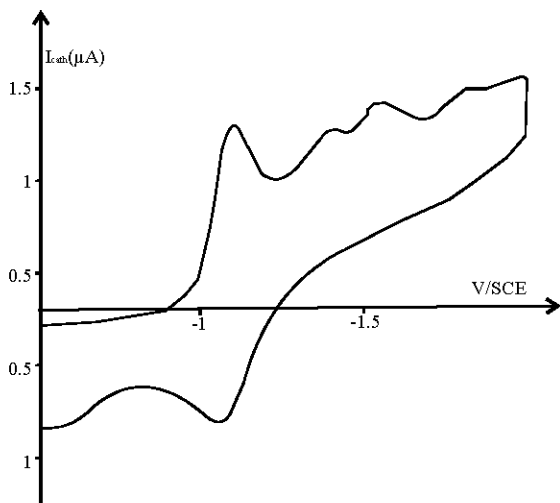The number of electron n, involved in an electrode reaction, was determined by a coulometric methode, for

Fig. 6: Cyclic voltammogram recorded at a mercury microelectrode in a DMF solution containing the coplex. Scan rate 5 V.s-1
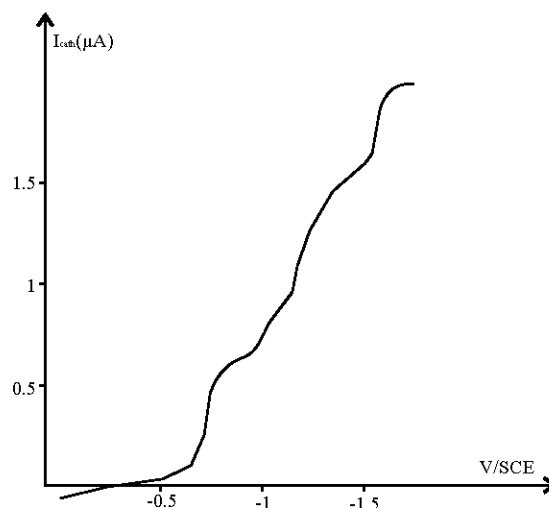

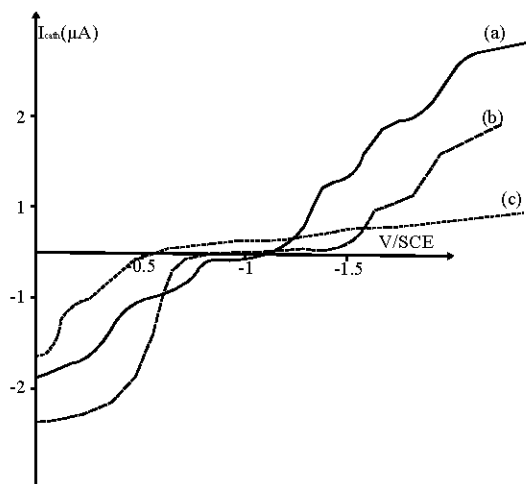Fig. 8: DC polarogram of the complex in PC /0.1 M TBAP

Fig. 7: Polarogram of (a) complex in DMF after total reduction at -1.1 V/SCE, complex in DMF reduced at -1.45 V/S, ligand reduced at -0.9 V/SCE
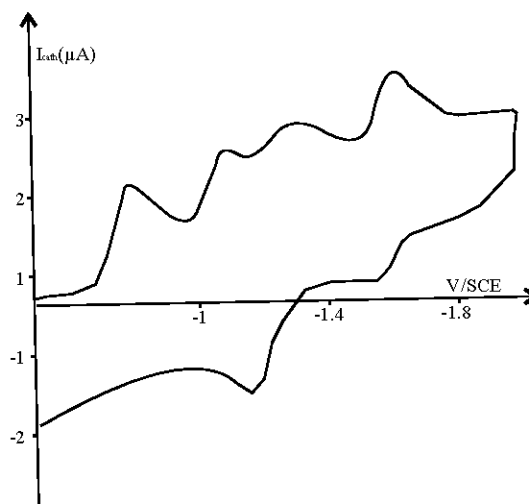

Fig. 9: Cyclic voltammetry of the complex in CP/ 0.1 MTBAP[v = 5 V.S⁻¹, scan between 0 and -2 V/SCE, electrode Hg]

the two first reduction steps. In each of the 2 steps, it is found that only 1 Faraday/mole of complex introduced in the solution is exchanged. Also, electrolysis performed at -1.4 V/SCE on complex solution gives 2 Faraday/mole exchanged for the overal double redution.

Both waves have limiting currents proportional to the analytical concentration of Uranyl complex and indicate that they were controlled by diffision.

Logarithmic analysis of the two waves results in straight lines with a slope, respectively for the first and the second, of 0.085 and 0.110 V. This data indicates that just the first step is close to reversible.

Figure 6 the cyclic voltammograms obtained on mercury electrode 0 to - 2 V/SCE show, as in polarography four cathodic peaks and one anodic in the reverse scan which was directly associated to the first peak.

The analysis of the cyclic voltammetric data for the first step shows the following features :

E^c_p and $E^c_p/2$ - E^c_p shift towards negative values as v increases; E^c_p-E^a_p increases with v; I^a_p / I^c_p progressively increases with v. These results reveal that the first electrode process is quasi-reversible, followed by a reversible chemical reaction, Since the second peak is malformed no analysis could be calculated, but the absence of the reoxydation peak associated to the second peak suggest that the process is irreversible
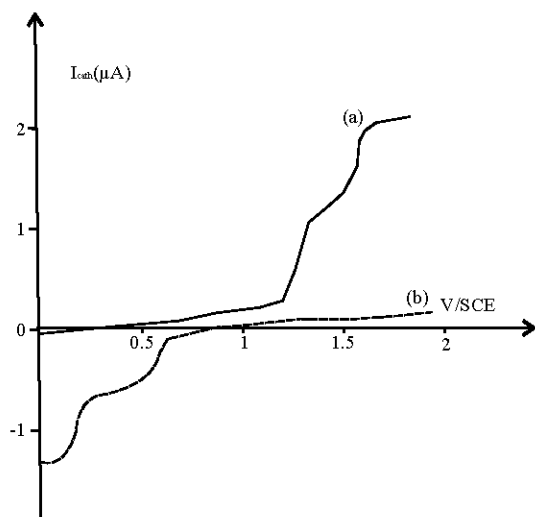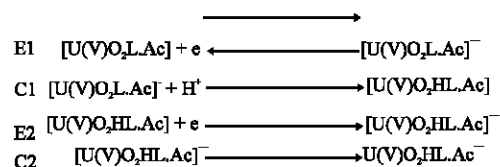
Fig. 10: Polarogram in PC/0.1M TBAP Complex after total
reduction at -1.1 V/SCE. Ligand reduced at - 1.7
V/SCE

Table 1: Relation between donor number and potential redox.

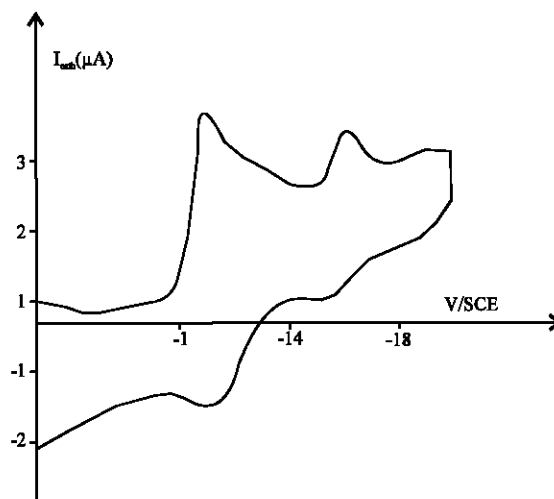| Solvent	D.N.	-$E^1_{1/2}$ (V/SCE)
DMSO	29.8	1.14
DMF	26.6	1.03
PC	15.1	0.75

Fig. 11: Voltammogram of the complex in PC with the
presence of Increasing amounts of added DMSO
(drop time 2 s)

The polarogram of the uranyl complex solution in
DMF (Fig. 7), after a complete reduction at - 1.1 V/SCE
shows the absence of the first wave and the apparition of
two anodic waves at -0.7 and -0.35 V/SCE. The same
solution is totally reduced at -1.45 V/SCE and shows in
polarography an important anodic signal at -0.5 V/SCE.

Solution ligand totally reduced at -1.9 V/SCE
presents in polarography 2 anodic waves at -0.1 and -0.4
V/SCE. After this we can say that the first chemical
reaction can't be a destruction of the complex.

On the basis of this results and if we take in
consideration the presence of H^+ in DMF, the reduction of
the uranyl complex is shown in scheme 2.

Scheme 2:

E1 [U(V)O$_2$L.Ac] + e ⇌ [U(V)O$_2$L.Ac]$^-$

C1 [U(V)O$_2$L.Ac]$^-$ + H$^+$ ⟶ [U(V)O$_2$HL.Ac]

E2 [U(V)O$_2$HL.Ac] + e ⟶ [U(V)O$_2$HL.Ac]$^-$

C2 [U(V)O$_2$HL.Ac]$^-$ ⟶ U(V)O$_2$HL.Ac$^-$

Propylene Carbonate (PC): Complex in PC schows in dc
polarography four waves with half-wave potential of -
0.75; - 1.03; - 1.2 and - 1.6 V/SCE (Fig. 8). Ligand in PC
gives one polarographic wave at 1.62 V/SCE which
indicates that the tast polarographic wave from the
complex is due to the reduction of the ligand.

For the first wave plat of Log[i/id - i]versus E, is
linear. The slope of this linear plot is 0.10 V. As the
formal slope of such representation is 0.059/n (V.). The

observed value of 0.10 V indicates that the first reduction
is irreversible (slow electron transfer).

The typical voltammogram is given in Fig. 9. The
reduction peak potential E^{c1}_p, E^{c2}_p and E^{c3}_p correspond to
the reduction of uranyl ion complex. On the backward
scan, one anodic peak (E^a_p) are observed at all scan rates
(2-100 V.s^{-1}).

The peak E^a_p corresponds to the reduction peak E^{c3}_p,
the difference $\Delta E_p = E^{c3}_p$-E^a_p being about 70 mV at low
scan rates (2. V.s^{-1}). These results indicate that only the
third reduction step has a reversible character and they
support the hypothesis that a chemical step is interposed
between the second and the third chemical reduction
steps of complex.

Coulometric electrolysis at constant potential have
been carried out on the complex, for each of the three
observed reduction steps. In each one it is found that one
electron is exchanged.

These results, as well as the specific chareacteristics
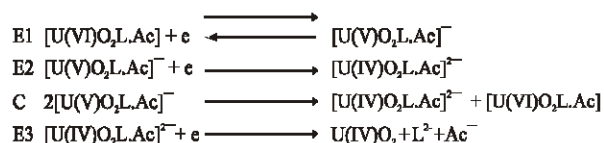in the chemistry of uranium, led us to examine the
polarographic behaviour after electrolyses.

Solution of the complex are totally reduced in PC at
-1.1 V/SCE, Fig. 10 illustrates the changes induced on a
polarogram. The only difference was the absence of the
two first waves, this result indicates the no reoxydation of
the species formed after the two first reductions. The

same experience is repeated on ligand solution at -1.7 V/SCE which presents two anodic waves at - 0.1 and - 0.5 V/SCE.

The results of the electroreduction of the uranyl complex in PC shows that the half-wave of the first stepare less negative than in DMSO and in DMF, which is due to weak of donor number. The above results lead us to scheme III in which the Chemical step (C) is the disproportionation.

Scheme 3:

E1 $[U(VI)O_2L.Ac] + e \longrightarrow [U(V)O_2L.Ac]^-$
E2 $[U(V)O_2L.Ac]^- + e \longrightarrow [U(IV)O_2L.Ac]^{2-}$
C $2[U(V)O_2L.Ac]^- \longrightarrow [U(IV)O_2L.Ac]^{2-} + [U(VI)O_2L.Ac]$
E3 $[U(IV)O_2L.Ac]^{2-} + e \longrightarrow U(IV)O_2 + L^{2-} + Ac^-$

The data obtained show that uranyl complex is reduced differently in each solvents.
The potential of U(VI)/U(V) couple shifts towards negative potential value with increasing electron-pair donor properties of the solvent (Table 1).

In order to put evident this hypotheses, we have analyzed the influence of the addition of DMSO on the complex solution in PC. Figure 11 illustrates the changes induced on the voltammogram of complex in PC when adding amount (6%) of DMSO.

The new reversible peak at - 1.15 V/SCE which looks like the voltammogram of complex in DMSO, this result show the presence of DMSO further the formation of the new complex like [U(V)O$_2$L.Ac. 3DMSO] and we can illustrate reduction of the complex in DMSO as:

Scheme 4:

$[U(VI)O_2L.Ac.3DMSO] + e \rightleftharpoons [U(V)O_2L.Ac.3DMSO]^-$
$[U(V)O_2L.Ac.3DMSO]^- \longrightarrow [U(V)O_2L.Ac.3DMSO] + L^-$
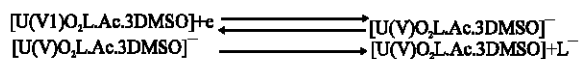
CONCLUSION

The effect of solvent on a physico-chemical quantity is represented by relation ship involving empirical parameters, which describe the main contribution of the solvent influence on the quantity involved (Krygowsky and Fawcett, 1975). One of the most used empirical parameters in the description of solvent effects on redox potentials is the Gutmam donor number, DN (Gutman and Wychera, 1966) which was chosen as a measure of solvent Lewis basicity. Extended studied have shown that the redox potential shifts to more negative potentials with increasing Lewis basicity of the solvents.

In DMSO, a decomplexation reaction is observed after the first reduction step, however in DMF and PC we can attempt uranium (IV).

The solvation process of uranyl (VI) complex in the various solvents is responsible of the difference behaviour of the complex.

As a final consideration it seems that the increasing Lewis basicity of solvents favours the inner-sphere structure reorganization of the electronically active complex.

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