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Polarographic Investigations on Uranyl(VI) Complexes in Dimethylsulfoxide.
1. Monocarboxylic Ligands

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*The formation of acetate, glycolate, chloroacetate and β-chloropropionate complexes of uranium(VI) in dimethylsulfoxide has been investigated by the polarographic method. 0.1*M *tetrabutylammonium perchlorate was used as supporting electrolyte. The 3:1 acetate and the 1:1 glycolate complexes give distinct cathodic waves; the polarographic behaviour allows to evidentiate also the 1:1 and 2:1 acetate, the 1:1 chloroacetate and β-chloropropionate complex formation. The formed complexes are stronger in DMSO than in water and the more so the harder the ligand. The (a)-character of uranyl ion is more marked in DMSO than in aqueous media.*

Introduction

Until now the uranium coordination chemistry in aprotic solvents has not been extensively studied in respect to aqueous media. This fact is partly due to the small number of available techniques in these solvents. In view of this circumstance a series of investigations concerning the coordination chemistry of uranyl ion in aprotic solvent has been undertaken using the polarographic method which provides a useful, though not very accurate, method to investigate complex formation.

The aim of these studies is to point out the solvent effect on some complex formation reactions involving uranyl ion and donors of different bonding characteristics.

As previously reported [1, 2] dimethylsulfoxide (DMSO) is a suitable aprotic medium for polarographic measurements on uranium(VI); further Ahrland *et al.* [3, 4] have recently published potentiometric and enthalpimetric data on metal halide and pseudohalide complexes in this solvent.

The present paper deals with the complex formation between dioxouranium(VI) ion and acetate, chloroacetate, β-chloropropionate and glycolate ions.

Experimental

Chemicals

Reagent grade dimethylsulfoxide (DMSO) was purified by distillation at reduced pressure [5].

Reagent grade $UO_2(NO_3)_2 \cdot 6H_2O$ was converted to $UO_2(NO_3)_2 \cdot 5$ DMSO by refluxing with an excess of DMSO at reduced pressure at 60 °C for 8 hours [6]; the DMSO-solvate was hence crystallized and the yellow product dried in a vacuum oven at 50 °C.

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

Tetrabutylammonium acetate (TBAAc), chloroacetate (TBAAcCl) glycolate (TBAGly) and β-chloropropionate (TBAPrCl) were prepared by neutralizing known amounts of the reagent grade acids with tetrabutylammonium hydroxide; the water was removed under vacuum, the white products dissolved in anhydrous methanol and finally crystallized. TBAAcCl, TBAPrCl and TBAGly are hygroscopic and the crystallization from methanol was very difficult; their water content, evaluated by Karl–Fisher titration, was of the order of 3%. To minimize the hydration process of the salts, concentrated stock solutions in DMSO were prepared.

Apparatus and Methods

Polarographic curves 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. A saturated calomel electrode (SCE) was used as reference; the auxiliary electrode was a platinum foil; the working electrode was a conventional dropping mercury electrode with a mechanical control of drop time.

Coulometric measurements were performed with an Amel potentiostat Mod. 551, with an associated electronic integrator Amel Mod. 558, 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.

A Karl–Fisher titrator Mod. 232 Amel was employed in the evaluation of the water content of the salts.

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

In all tests 50 ml of 0.1*M* TBAP–DMSO supporting electrolyte were used.

The uranyl compound and TBAAc were added as weighed quantities, while TBAAcCl, TBAPrCl and TBAGly were added as known volumes from stock solutions.

Results and Discussion

The voltammetric and conductometric behaviour of uranyl ion in DMSO has been already reported [2].

In order to check the possible formation of polynuclear species some tests at different uranyl concentrations (in the range 2.10^{-4}–$2.10^{-3}M$) were carried out. The obtained data indicated that no appreciable effect had to be ascribed to the uranyl concentration. These results agree with previous reports in aqueous media [7].

Acetate

The addition of increasing amounts of TBAAc to the uranyl solution caused a progressive lowering of the uranium(VI) wave and a shift of its half-wave potential from –0.53V towards more negative potentials. This lowering was compensated by the appearance of two successive cathodic waves, the first of which slightly shifted from $E_{1/2}$ = –0.77V towards negative potential values at increasing ligand concentration. At the same time also an anodic process took place due to the anodic dissolution of the electrode to form stable mercury acetate complexes.

Controlled potential coulometric experiments carried out at potential values corresponding to the limiting current of the most cathodic process (–1.30V) at a molar ratio (Ac^-/UO_2^{2+}) of about 3.5/1 gave an n_e mean value of 1.1 [2].

In Fig. 1 the current trend of the observed cathodic processes against the molar ratio Ac^-/UO_2^{2+} is plotted. As can be noted the reduction process "a" (initial $E_{1/2}$ = –0.53V) can be detected up to a molar ratio of about 2.5/1. The second small cathodic wave "b" ($E_{1/2}$ = –0.78V) starts at a molar ratio of about 1/1, reaches its maximum value around the 1.5/1 molar ratio and finally disappears near to the 3/1 ratio. The third reduction process "c" ($E_{1/2}$ = –1.10V) takes place at about 1.5/1 ratio and reaches its highest value near to the 4/1 ratio, without further changes. The anodic wave appeared at about 1.5/1 ratio and continuously increased at increasing acetate additions; its $E_{1/2}$ value correspondingly shifted from –0.08V to more negative potentials.

Logarithmic analysis [E *vs.* $\log(i_d - i)/i$] of the cathodic waves "a", "b", "c" gave straight lines with slopes of 0.059V, 0.057V and 0.070V respectively. These data point out that the observed one-electron cathodic processes can be considered substantially reversible. On the contrary the shape and logarithmic analysis of the anodic wave indicated a rather complicated process.

The plot of $E_{1/2}$ values of the reduction process "a" against the logarithm of acetate concentration was curved. From it two tangents of integral slope could be clearly drawn, indicating (p – q) values of 1 and 2 respectively [8]. Since the studied cathodic processes correspond to a reduction of complexes to a lower oxidation state, according to the general scheme:

$$ML_p^{+n} + me^- \longrightarrow ML_q^{+(n-m)} + (p-q)\,L^-$$

the following equation can be used to evaluate the ratios of the stability constants of the oxidized and reduced forms, β_{Ox}/β_{Red}:

$$(E_{1/2})_{free} - (E_{1/2})_{complex} = \frac{RT}{nF}\ln(\beta_{ML_p}/\beta_{ML_q}) + (p-q)\frac{RT}{nF}\ln[L^-]$$

Owing to the established poor coordinating ability of uranium(V) [9] the (p – q) value of 1 can be interpreted in terms of formation of the 1:1 uranium(VI) acetate complex and no formation of uranium(V) complexes (q = 0). In this case the ratio of stability constants resulted to be:

$$\frac{\beta_{Ox}}{\beta_{Red}} = 8.10^3$$

where β_{Ox} refers to the 1:1 uranium(VI) acetate complex and β_{Red} to the uranium(V) DMSO complex. Likewise the (p – q) value of 2 should indicate the coordination of a second acetate group.

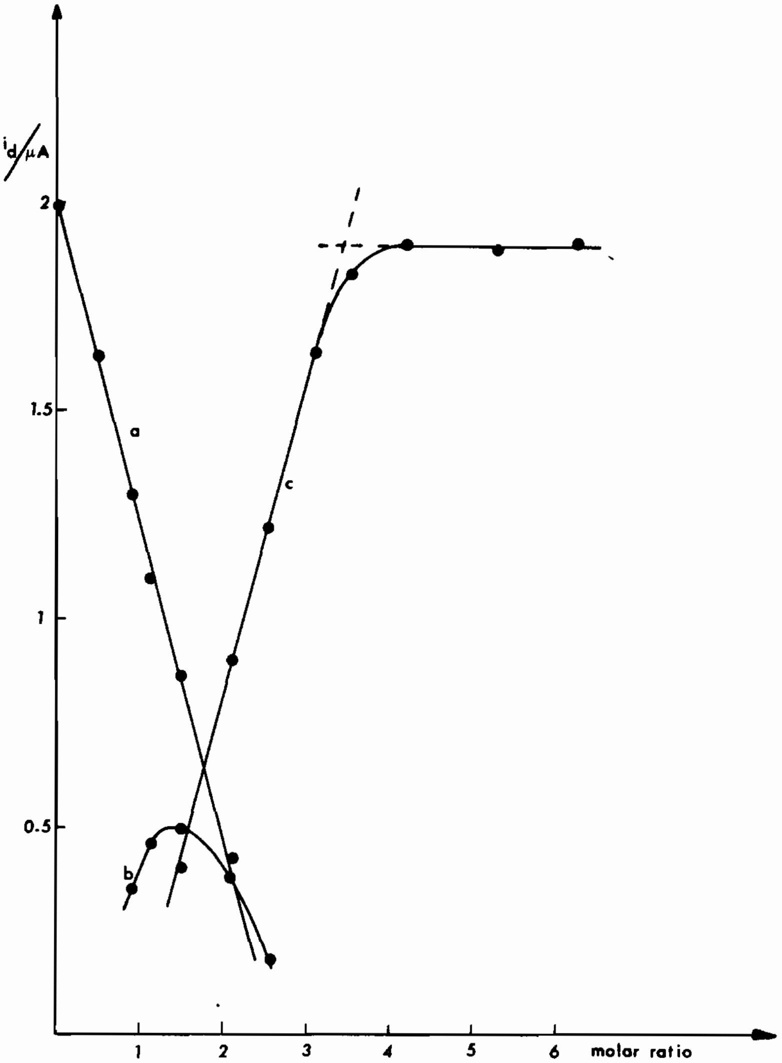

Figure 1. Current trend of the polarographic reduction processes as a function of the molar ratio Ac^-/UO_2^{2+}. Uranium(VI) concentration: $9.65 \times 10^{-4} M$.

The shape of curve "c" in Fig. 1 evidentiates the almost quantitative formation of the 3:1 acetate uranium(VI) complex, while the existence of the 2:1 complex is suggested by curve "b", which exhibits a maximum current value between the disappearance of process "a" and the formation of the more stable 3:1 complex. In fact, at increasing acetate ligand concentration also uranium(V) complexes must be formed, and the process "b" should correspond to the 2:1 uranium(VI) together with the 1:1 uranium(V) acetate complex formation.

In the case of process "c" no shift in half-wave potential was observed (p = q), hence the ratio of the stability constants of the oxidized and reduced forms can be evaluated through the simplified equation:

$$\Delta E_{1/2} = \frac{RT}{F} \ln \frac{\beta_{Ox}}{\beta_{Red}}$$

The obtained value was:

$$\frac{\beta_{Ox}}{\beta_{Red}} = 5.10^9$$

where β_{Ox} and β_{Red} refer to the 3:1 acetate–uranium complexes.

As expected the stability constants values confirm the higher coordinating ability of uranium(VI) species over the uranium(V) one. Furthermore the quantitative formation of the 3:1 complex well agrees with the hexacoordination of uranyl ion on the equatorial plane accomplished by the three acetate ions, which act as bidentate ligands *via* the two oxygen atoms.

Glycolate

Additions of TBAGly stock solution to the uranyl caused the lowering of the cathodic wave of uranium-

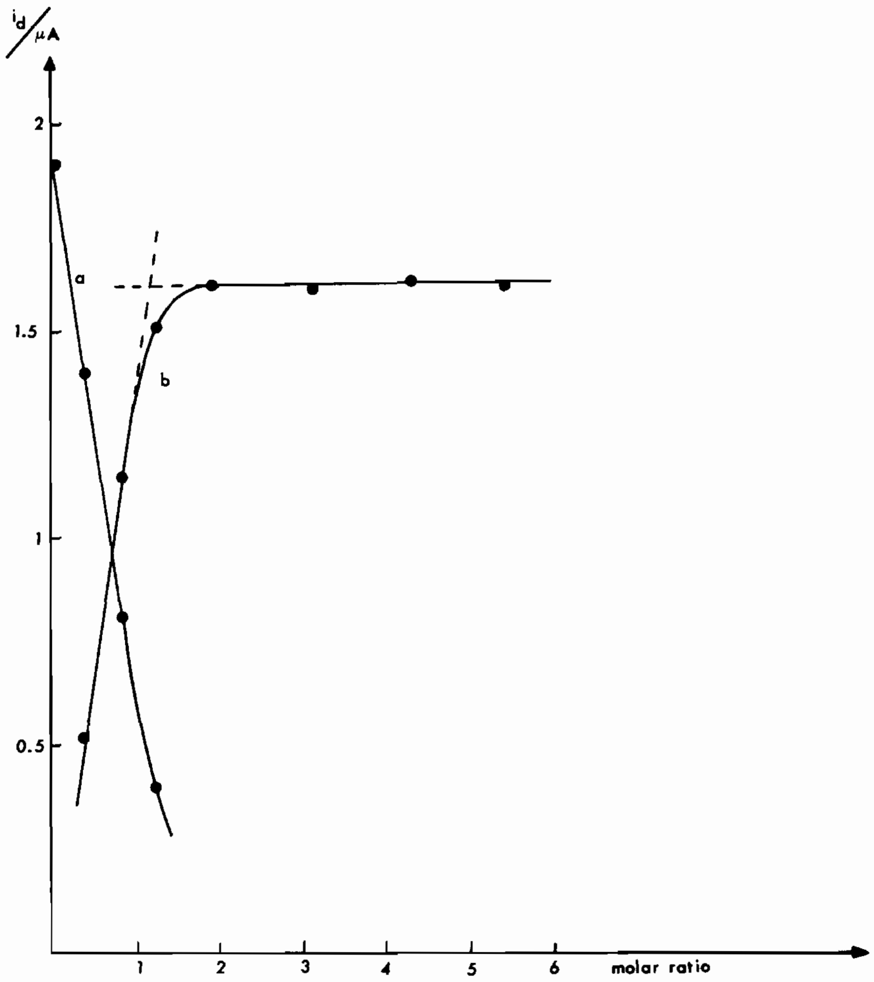

Figure 2. Current trend of the cathodic processes as a function of the molar ratio Gly^-/UO_2^{2+}. Uranium(VI) concentration: 8.68 × $10^{-4}M$.

(VI); in correspondence a new cathodic process appeared, the half-wave potential of which remained unchanged up to a molar ratio (Gly^-/UO_2^{2+}) of about 2/1 ($E_{1/2}$ = −0.89V) and shifted towards more negative values beyond this ratio. At the same time an ill-shaped anodic wave arises, involving the formation of stable mercury glycolate complexes.

Coulometric data performed at −1.1V in solutions containing glycolate and uranyl ions in the molar ratio 2/1, indicated that one mol of electrons per mol of uranium(VI) was involved.

Fig. 2 shows the current trend of the cathodic processes as a function of the molar ratio Gly^-/UO_2^{2+}. It can be noted that the uranyl reduction current "a" decreases up to the ratio 2/1, while the current of the uranyl glycolate complex, "b", increases, reaches its maximum value near to the 2/1 ratio and then remains constant. Logarithmic analysis of the wave of the uranyl complex "b" revealed a reversible one-electron behaviour up to the molar ratio 2/1 and then progressively departed from the reversible value.

The following ratio of the stability constants of the glycolate complex has been obtained:

$$\frac{\beta_{Ox}}{\beta_{Red}} = 3.10^5$$

The trend of Fig. 2 does not allow us to state surely if β_{Ox} and β_{Red} have to be referred to the 1:1 or 2:1 uranium glycolate complexes.

At ratios higher than 2/1 the plot of $E_{1/2}$ values *vs.* the logarithm of the glycolate concentration gave a straight line with a slope of 145 mV, indicating a (p − q) value slightly higher than 2 and suggesting the formation of higher uranium(VI) complexes. The lack of reversibility of this cathodic wave prevented any reliable evaluation of the stability constants of these successive complexation steps.

Chloroacetate

The additions of TBAAcCl stock solution to the uranyl caused the progressive shift of the cathodic

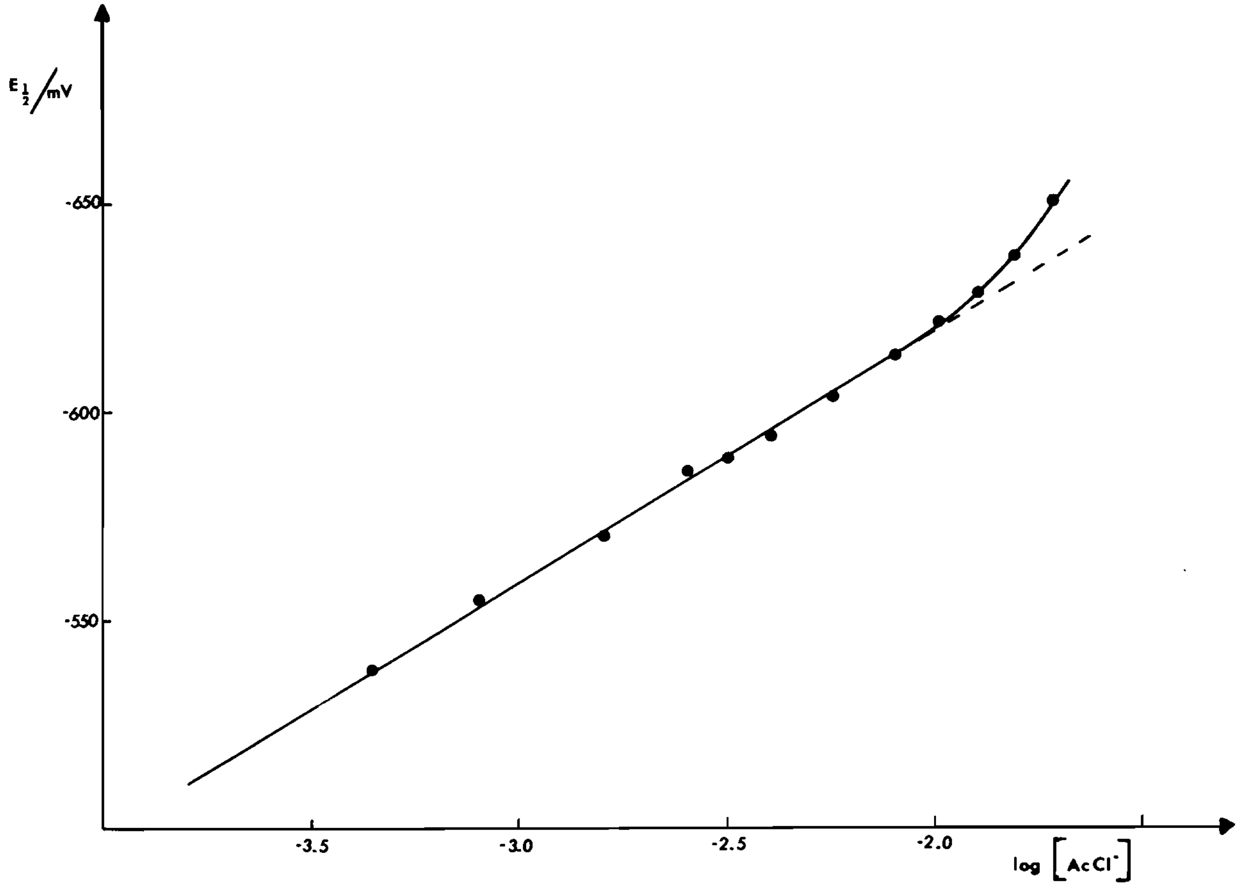

Figure 3. Plot of $E_{1/2}$ values of the cathodic wave as a function of the logarithm of the chloroacetate concentration.

wave of uranium(VI) ($E_{1/2} = -0.53V$) towards more negative potential values, without the appearance of any distinct cathodic process. Also an anodic wave appeared. Logarithmic analysis of the cathodic wave showed a slope of 0.064V suggesting a reversible one-electron process.

In Fig. 3 the $E_{1/2}$ values of the reduction process against the logarithm of the chloroacetate concentration are plotted. The experimental data lie quite well on a straight line, excepting the points at higher concentration which lie above. The straight line gives a slope of 60 mV. This result clearly indicates a (p – q) value of 1 and suggests the formation of the 1:1 complex, in the hypothesis that the uranium(V) species does not form a stable complex.

The above straight line allows us to calculate the ratio between the stability constants:

$$\frac{\beta_{Ox}}{\beta_{Red}} = 3.10^3$$

The upward curvature at high ligand concentrations demonstrates the existence of successive complexation steps also in this case.

β-Chloropropionate

The additions of TBAPrCl stock solution to the uranyl only caused a progressive shift of the cathodic wave of uranium(VI) towards more negative potentials. Also in this case an anodic wave took place. Logarithmic analysis of the wave of the reduction process gave a straight line with a slope of 0.063V, suggesting a reversible one-electron process.

The plot of the $E_{1/2}$ values of the cathodic wave *vs.* the logarithm of the β-chloropropionate concentration is reported in Fig. 4. As can be noted, the curve fits well two straight segments, the slopes of which (58 and 114 mV respectively) give (p – q) values of 1 and 2. As discussed above, these data suggest the formation of 1:1 and 2:1 $PrCl^-/UO_2^{2+}$ complexes.

The calculated ratio of the stability constants relative to the first step is:

$$\frac{\beta_{Ox}}{\beta_{Red}} = 3.10^3$$

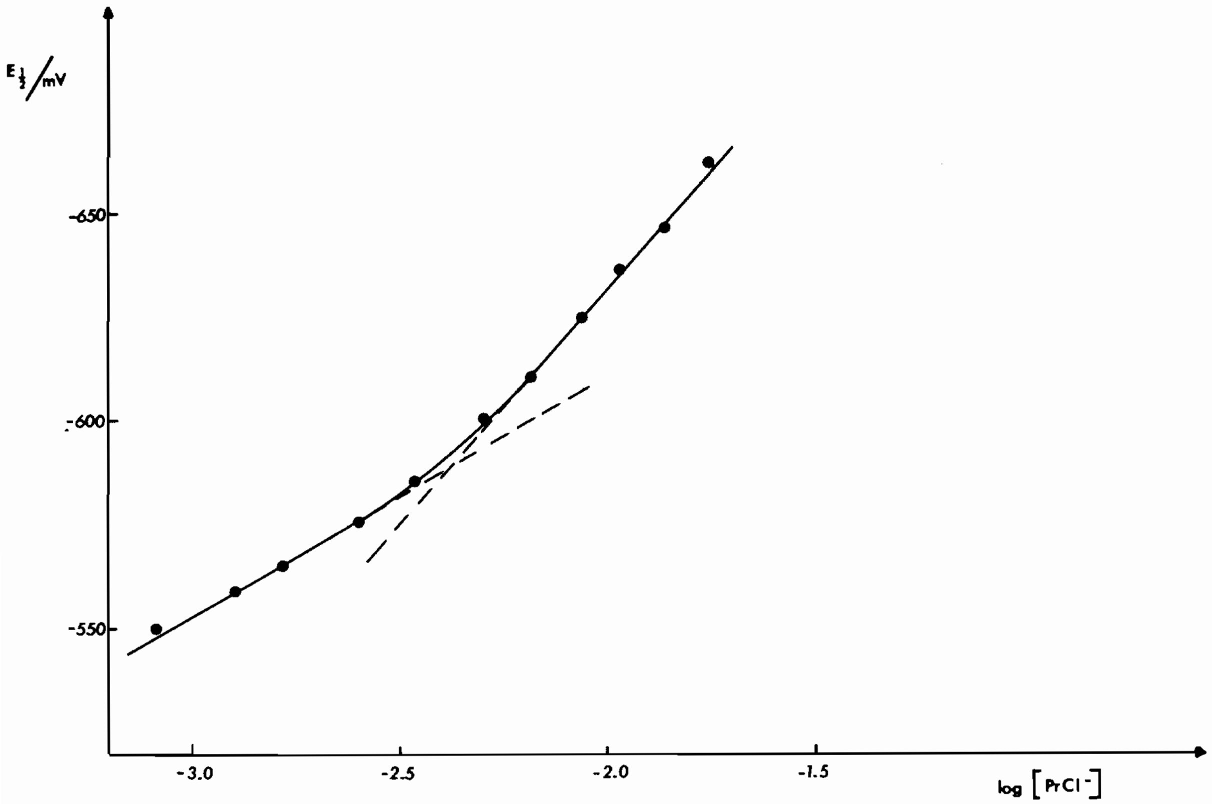

Figure 4. Plot of $E_{1/2}$ values of the cathodic wave as a function of the logarithm of the β-chloropropionate concentration.

TABLE I. Stability of 1:1 Uranyl Monocarboxylate Complexes in DMSO and Water.

		CH_3COO^-	$CH_2ClCH_2COO^-$	CH_2ClCOO^-
DMSO	$\log \frac{\beta_{Ox}}{\beta_{Red}}$	3.9	3.5	3.4
Water	$\log \beta_1$	2.4	2.0	1.4

Conclusions

From the above results some correlations about the relative stabilities of the tested complexes can be deduced.

At first the general behaviour of the complexes might indicate that the involved uranyl(VI) glycolate species is the 1:1 complex. In this connection the β_{Ox}/β_{Red} value shows that the 1:1 uranyl glycolate complex is more stable than the corresponding acetate complex in spite of the basicity of the ligand. This fact is not surprising since it was also observed in aqueous medium [12, 13]. In DMSO it appears more evident.

Glycolate ion must act as a chelating agent *via* the carboxylate and the hydroxy groups in the formation of the first complex species; the stability of the successive steps cannot be very high since distinct new cathodic waves were not observed. The coordination of successive glycolate ions probably causes the breaking of the hydroxy-uranyl bond and the stability of the formed complexes would again depend on the ligand basicity.

Furthermore the results suggest that the maximum number of monocarboxylate ligands linked to uranyl(VI) ion is three, in agreement with reported literature data in aqueous media [7, 10–13].

In Table I the log β_{Ox}/β_{Red} values relative to the 1:1 uranium(VI) ligand complex together with $\log\beta_1$ ones from references [7, 10–13] are reported.

It can be noted that also in DMSO an increased stability at increasing basic properties of the monocarboxylate ion ($AcCl^-$, $PrCl^-$, Ac^-) is found. This finding agrees with the (a) or "hard" character of the uranyl ion acceptor, which forms complexes that are more stable the stronger the ligand basicities in protic solvents.

Finally it can be observed that the stabilities of all studied complexes change with the solvent in that the complexes become much stronger in DMSO than in water, as already observed in the case of the "hard" acceptor zinc [4]. The stronger electrostatic interaction in DMSO, owing to its low dielectric constant value, should contribute to the increased stability of the complexes, but a stronger solvation of the metal ion must be also taken into account as a competitive effect. In this connection the solvation effect could be responsible for the β_{Ox}/β_{Red} differences among the studied monocarboxylate ligands, these ratios being lower in DMSO than in aqueous media.

Acknowledgements

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