Inorganica Chimica Acta, 27 (1978) 157–161

Polarographic Investigations on Uranyl(VI) Complexes in Dimethylsulfoxide.
III. Halides and Pseudohalides

P. ZANELLO, A. CINQUANTINI, G. A. MAZZOCCHIN
Institute of General Chemistry, University of Siena, Italy
O. TRAVERSO
Chemical Institute, University of Ferrara, Italy
Received July 18, 1977

The polarographic study of the uranyl(VI)–halides complexes in DMSO showed the formation of $[UO_2F_2]$ *and* $[UO_2Cl]^+$ *stable species, while bromide and iodide ions do not form stable uranium(VI) complexes, in agreement with the "hard" character of uranyl(VI) ion.*

The complexes formation between pseudohalides and uranium(VI) evidentiated the following species, stable enough to be polarographically revealed: $[UO_2(N_3)_3]^-$, $[UO_2(CN)]^+$ *and* $[UO_2(CN)_2]$; *on the contrary thiocyanate ion does not form sufficiently stable complex species in DMSO.*

Cyclic voltammetric tests were also performed to investigate the anodic dissolution process of mercury in the presence of azide ion.

Introduction

This paper, which is part of a series concerned with the polarographic investigation on the complexes formation of uranium(VI) with donors of different coordinating tendencies in dimethylsulfoxide [1–3], is devoted to halide and pseudohalide ligands.

Investigations on the reaction between halides and pseudohalides and some metal ions in nonaqueous solvents have been reported [4–8]. As regards uranium(VI) the formation of its fluorido [9], chlorido [10, 11], thiocyanato [12] and azido [13] complexes has been studied in aqueous media, but very few data are available in aprotic solvents [14].

In this connection the present paper reports a polarographic study of the complexation equilibria between dioxouranium(VI) ion and fluoride, chloride, bromide, iodide, cyanide, thiocyanate and azide ions in dimethylsulfoxide.

Experimental

The apparatus and the methods as well as preparation and purification of dimethylsulfoxide (DMSO), of the DMSO–uranyl(VI) solvate and of tetrabutylammonium perchlorate (TBAP) supporting electrolyte, have been already reported [1, 2].

The polarographic tests were carried out at 25 ± 0.1 °C and 0.1 *M* TBAP was used as supporting electrolyte.

Tetrabutylammonium bromide (TBABr) and iodide (TBAI) were Carlo Erba RS products.

Tetrabutylammonium chloride (TBACl) of highest purity was a Fisher Scientific Company product.

Tetrabutylammonium fluoride (TBAF) was prepared by neutralizing a known amount of tetrabutylammonium hydroxide with hydrofluoric acid; the water was removed under vacuum, the white product dissolved in anhydrous methanol and finally crystallized. The crystallization from methanol was very difficult and the final product was hygroscopic; its water content, evaluated by Karl–Fisher titration was of the order of 5%.

Sodium cyanide, ammonium thiocyanate and sodium azide were reagent grade Carlo Erba products.

Results and Discussion

The voltammetric characteristics of uranyl(VI) ion in DMSO have been previously reported [1] and the absence of polynuclear species in the tested experimental conditions has been checked [2].

Fluoride

The addition of TBAF to the uranyl(VI) solution caused the lowering of the uranium(VI) wave ($E_{1/2}$ = –0.53V) and the appearance of a cathodic wave at an half-wave potential of –0.80V. At the same time also an anodic wave took place due to the formation of stable mercury complexes [15].

In Fig. 1 the trend of the cathodic currents relative to the cited processes is reported.

Coulometric tests carried out at a controlled potential of –1.0V on solutions containing TBAF and uranyl(VI) in the molar ratio 2/1 gave a n_{e-} value of 1.1 [1].

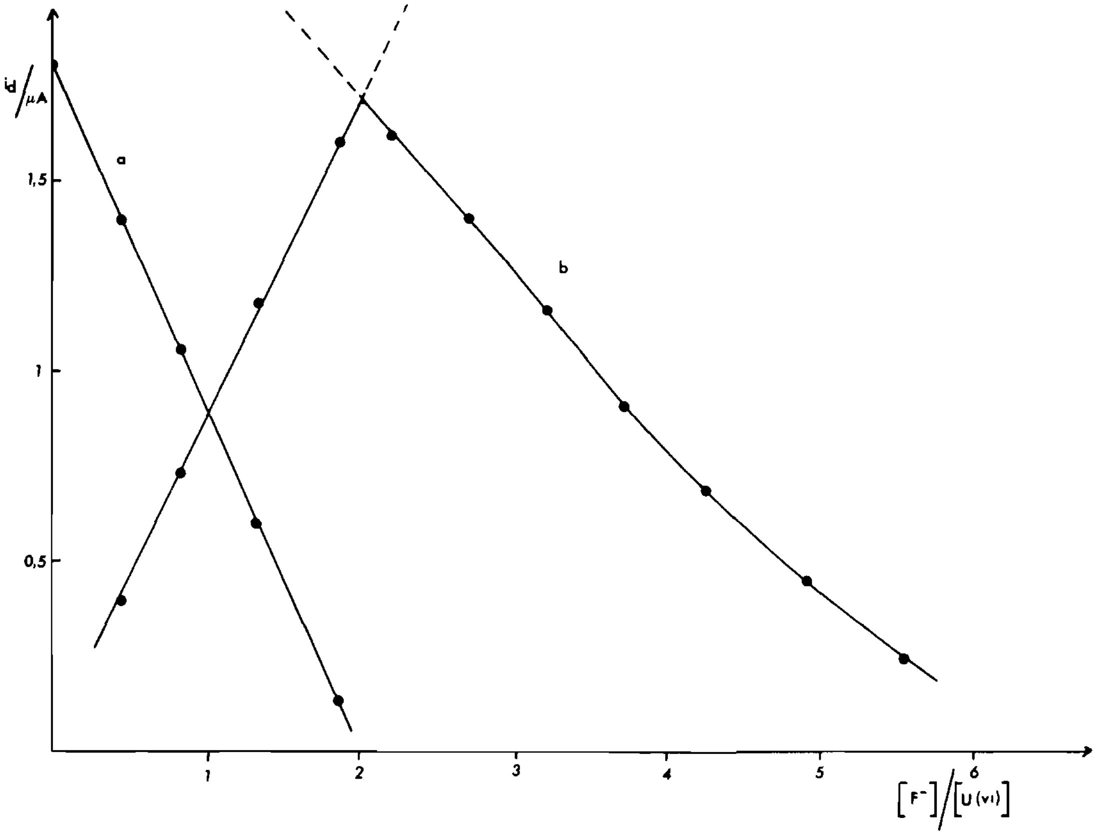

Figure 1. Current trend of the polarographic reduction processes as a function of the molar ratio F^-/UO_2^{2+}. Uranium(VI) concentration; 8.57×10^{-4} *M*.

Logarithmic analysis of the wave relative to the process "b" gave a straight line with a slope of 0.061V indicating a one-electron reversible polarographic process.

The picture of Fig. 1 clearly evidentiates the quantitative formation of the 2:1 fluoride–uranyl(VI) complex; in fact the free uranium(VI) current (process "a") linearly decreases coming to an end at the 2/1 ratio, while the process "b" increases and reaches its maximum current value near to the 2/1 ratio.

The appearance of a distinct polarographic wave for the uranium(VI) complex in this medium suggests that the rate of formation and dissociation of the complex is much lower than the rate of its diffusion towards the electrode surface.

Further addition of TBAF complicates the complex formation processes as the solution starts to fade, wave "b" decreases and its half-wave potential more and more shifts towards negative potential values. In addition the irreversible process related to the reduction of uranyl(VI) to uranium(IV) [1, 16] shifts towards more positive potentials. These findings may by interpreted as follows: the decrease of wave "b" indicates the formation of apparently colourless successive fluoride–uranium(VI) complexes; the reduction processes relative to these higher complexes are however masked by the reduction to uranium(IV) which is notably favoured in the presence of fluoride ion according to the well known stability of uranium(IV) fluoride complexes [17]. At any rate, we did not think it necessary to investigate the nature of the processes occurring at so negative potential values, owing to the irreversibility of the polarographic processes and the unavoidable presence of traces of water which produces its effects in this potential range [16].

By considering the process "b" up to concentrations where no $E_{1/2}$ shift occurs, it is possible to calculate the ratio of the stability constants of the oxidized and reduced forms [1–3], which resulted:

$$\frac{\beta_{Ox}}{\beta_{Red}} = 4 \times 10^4$$

where β_{Ox} refers to the 2:1 fluoride–uranium(VI) complex, and β_{Red} refers to the 2:1 fluoride–uranium(V) complex.

Chloride

The addition of increasing amounts of TBACl to the uranyl(VI) solution only caused a progressive

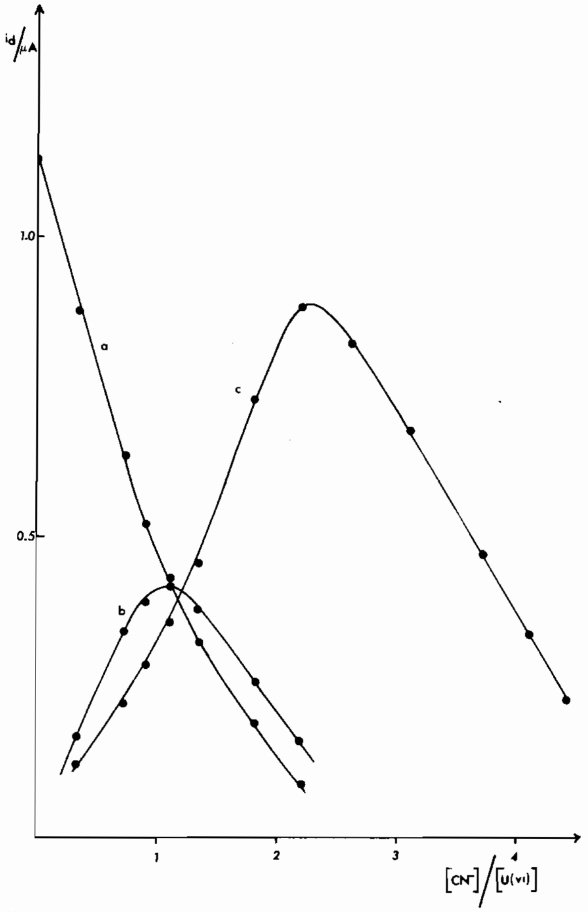

Figure 2. Current trend of the cathodic processes as a function of the molar ratio CN^-/UO_2^{2+}. Uranium(VI) concentration: 5.54×10^{-4} *M.*

shifting of the uranium(VI) reduction wave towards more negative potential values. Also in this case an anodic wave appeared, related to the formation of stable mercury complexes. Logarithmic analysis of the cathodic wave showed a slope of 0.062V, indicating a reversible one-electron process.

By plotting the $E_{1/2}$ values *versus* the logarithm of the chloride concentrations a straight line with a slope of 0.058V is obtained, indicating a (p – q) value of 1 [18]. This result does not provide an univocal information about the composition of the involved complexes, but taking into account the poor coordinating ability of uranium(V) ion [19] (*i.e.*, q = 0) it is likely that the 1:1 chloride–uranyl(VI) complex is formed. In this hypothesis the computed stability constants ratio, $\beta_{Ox}/\beta_{Red} = 2 \times 10^3$, can be considered as a β_1 value, since a (p – q) value of 1 suggests that β_{Ox} refers to the 1:1 uranium(VI) complex, while β_{Red} refers to the uranium(V)–DMSO solvated ion.

Bromide and Iodide

The cathodic wave of uranium(VI) was not affected by the addition of increasing amounts of TBABr and TBAI up to 15/1 halide/uranium(VI) ratios, indicating that bromide and iodide are not able to substitute the DMSO molecules around UO_2^{2+} ion. Also in these cases anodic waves related to mercury–halide complexes were observed.

Cyanide

Uranium(VI) solutions containing increasing amounts of cyanide ion gave the reduction current trend reported in Fig. 2. Also the well-known anodic wave of stable cyanide–mercury complexes took place [20]. As can be noted, the free uranium(VI) limiting current ("a") decreases and a second reduction process ("b") appears, followed in its turn by a well defined third one ("c"). At cyanide/uranium(VI) ratios higher than 2/1 there was observed the appearance of a precipitate in the bulk of the solution, which does not redissolve at increasing cyanide concentrations.

The half-wave potentials of the waves corresponding to the second and to the third cathodic processes remained constant at –0.82V and –1.07V respectively; logarithmic analysis of these waves gave straight lines with slopes of 0.065 and 0.066V respectively, indicating one-electron almost reversible charge transfer processes.

The trend of Fig. 2 shows that in the tested experimental conditions two prevailing complex species forms: $[UO_2(CN)]^+$ and $[UO_2(CN)_2]$; the 1:1 complex is however less stable than the neutral 2:1 sparingly soluble complex, as evidentiated by the higher value of the limiting current of the process "c".

The $E_{1/2}$ value of process "c" allows to calculate the relative ratio of the stability constants of the oxidized and reduced forms; this ratio resulted:

$$\frac{\beta_{Ox}}{\beta_{Red}} = 1 \times 10^9$$

where β_{Ox} and β_{Red} refer to the 2:1 ligand–uranium complex.

Thiocyanate

The addition of increasing amounts of thiocyanate ion to the uranyl(VI) solution up to $SCN^-/U(VI)$ molar ratio of 30 caused neither significative lowering of the uranium(VI) cathodic wave nor appreciable shift in the $E_{1/2}$ value; this result indicates that the solvation of uranyl(VI) acceptor by DMSO is not affected by the thiocyanate ion.

Azide

The addition of increasing amounts of azide ion to the uranyl(VI) solution caused the progressive shift of

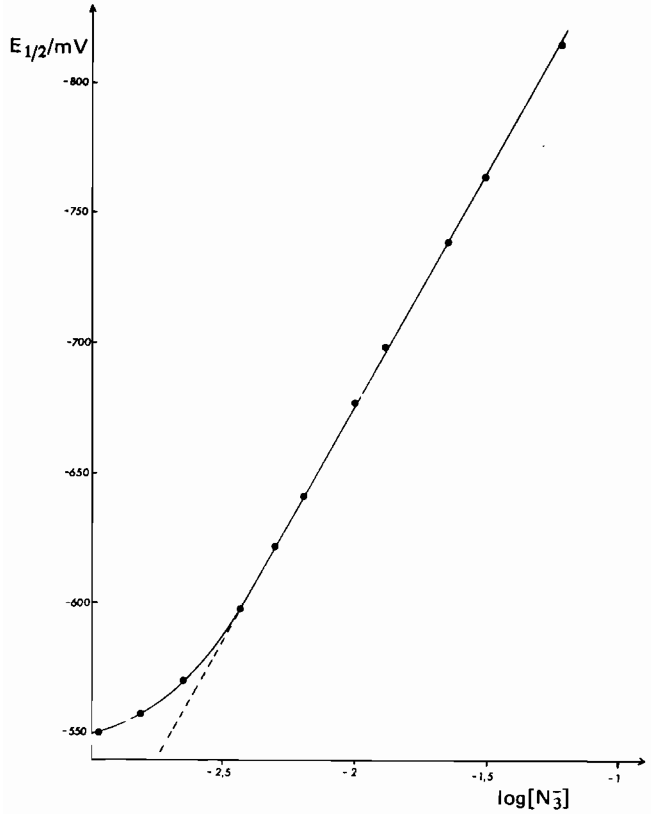

Figure 3. Plot of $E_{1/2}$ values of the cathodic wave as a function of the logarithm of the azide concentration.

the cathodic wave of uranium(VI) towards negative potential values, without the appearance of new distinct cathodic processes. On the contrary a very well-formed anodic process took place, due to the formation of mercury–azide complexes.

Logarithmic analysis of the cathodic wave recorded on solutions containing ligand and uranium(VI) at a ratio of 6:1 gave a slope of 0.058V, indicating a reversible one-electron process.

In Fig. 3 the plot of the $E_{1/2}$ values of the cathodic wave *vs.* the logarithm of the azide concentration is reported. The data lie on a straight line except for the points at lower concentrations, which lie above. The slope of the straight line is 177 mV, indicating a (p – q) value of 3. By considering again the poor coordinating ability of uranium(V) and by analogy with the data reported on uranyl(VI)–azido complex in aqueous media [13], this result suggests the prevailing formation of the complex $[UO_2(N_3)_3]^-$. The upward curvature at low ligand concentration indicates also the existence of lower complexation steps.

From the above straight line the β_{Ox}/β_{Red} ratio was calculated:

$$\frac{\beta_{Ox}}{\beta_{Red}} = 3 \times 10^8$$

β_{Ox} and β_{Red} refer to the 3:1 azide–uranium complex; this value confirms the poor coordinating ability of uranium(V) in respect to that of uranium(VI).

Since the anodic wave due to the mercury dissolution in the presence of azide is well formed we thought to gain quantitative information on this process; in fact such a behaviour has been studied until now only in aqueous media [21, 22].

0.1*M* TBAP–DMSO solutions containing N_3^- concentrations ranging from 2.0×10^{-4} to 6.2×10^{-3} *M* gave anodic waves of linear increasing height at constant $E_{1/2}$ value of +0.05V. Logarithmic analysis of this wave provided a slope of 60 mV.

Cyclic voltammetric curves recorded on these solutions revealed, however, that the electrode process is more complicated than that deducible from the only polarographic data. As can be seen from Fig. 4, at low scan rates (20–50 mV s^{-1}), a sharp peak following the diffusion controlled response is present in the reverse potential scan; the sharp peak disappears at higher scan rates (≥100 mV s^{-1}). In addition a noticeable shift of the E_p^a value with the scan rate has been observed and the $i_p/v^{1/2}$ value decreased with increasing scan rate; correspondingly the ΔE_p value ($E_p^a - E_p^c$) strongly increased.

All these data suggest that in DMSO the anodic dissolution of mercury in the presence of oxide ion

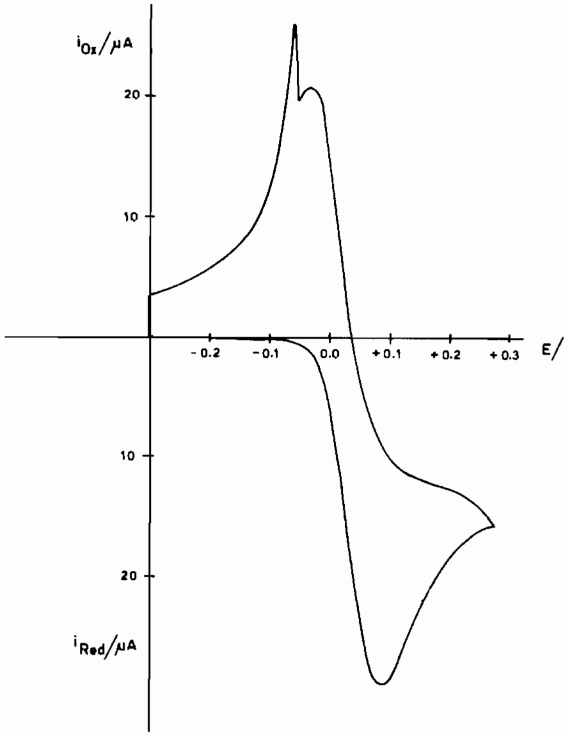

Figure 4. Cyclic voltammetric curve recorded with a mercury microelectrode on a 0.1 *M* TBAP, 1.2×10^{-3} *M* azide, DMSO solution. Scan rate: 50 mV s^{-1}. Anodic scan.

involves the slow formation of a precipitate on the electrode surface; a similar behaviour has been observed also in aqueous media [22]. Therefore the polarographic data cannot be directly used to evaluate quantitatively the complex formation steps between mercury and azide.

Conclusions

As pointed out by Pearson [23] and Ahrland [5], ligands able to participate in hydrogen bonding in protic media should form complexes relatively more stable in DMSO than in water.

The obtained data for halides well agree with the above suggestions in that the fluorido complex is much stronger than the chlorido one, while bromide and iodide ions do not form uranyl(VI) complexes stable enough to be revealed by the employed polarographic method.

Our β value ratios cannot be compared with literature data in aqueous media, owing to the absence of the β values for uranium(V) complexes, except for those of the 1:1 complex which can be considered β_1 values. In this connection it can be noted that the species $[UO_2Cl]^+$ shows a greater stability in DMSO than in water, where a β value of 1.06 M^{-1} [11] and 43.8 M^{-1} together with 680 M^{-1} in 90% EtOH medium [10] is reported. A similar result has been also obtained for the hard acceptor Zn(II) by Ahrland and Bjork [4].

The expected pattern for pseudohalide donors with soft acceptors is: $N_3^- < SCN^- < CN^-$ [24]. Our results do not allow to establish a clear inversed pattern for hard acceptors, owing to the different prevailing complex species, but undoubtedly they allow to evidentiate that SCN^- ligand forms less stable complexes than CN^- and N_3^- in DMSO solvent.

Although the present polarographic method provides only stability constant ratios, in agreement with previous data [1–3] all the formed uranyl(VI) complexes are much stronger in DMSO than in water, and uranyl(VI) exhibits a marked "a" character in DMSO solvent.

Acknowledgements

We are indebted to Mrs. G. Montomoli and Mr. F. Brogi for laboratory assistance. This work was supported by the Laboratorio di Chimica e Tecnologia dei Radioelementi, CNR (Padova).

References

1 P. Zanello, A. Cinquantini and G. A. Mazzocchin, *Inorg. Chim. Acta, 21,* 195 (1977).
2 P. Zanello, A. Cinquantini, P. Di Bernardo and L. Magon, *Inorg. Chim. Acta, 24,* 131 (1977).
3 A. Cinquantini, P. Zanello, G. A. Mazzocchin and O. Traverso, *Inorg. Chim. Acta, 25,* 141 (1977).
4 S. Ahrland and N. O. Bjork, *Acta Chem. Scand., A30,* 265 (1976).
5 S. Ahrland and N. O. Bjork, *Coord. Chem. Rev., 16,* 115 (1975).
6 S. Ahrland, N. O. Bjork and R. Portanova, *Acta Chem. Scand., A30,* 270 (1976).
7 V. Gutmann and W. K. Lux, *J. Inorg. Nucl. Chem., 29,* 2391 (1967).
8 V. Gutmann and H. Bardy, *Z. Anorg. Allg. Chem., 361,* 213 (1968).
9 S. Ahrland and L. Kullberg, *Acta Chem. Scand., 25,* 3457 (1971).
10 J. D. Hefley and E. S. Amis, *J. Phys. Chem., 64,* 870 (1960).
11 F. T. Bunus, *J. Inorg. Nucl. Chem., 36,* 917 (1974).
12 S. Ahrland, *Acta Chem. Scand., 3,* 1007 (1949).
13 F. G. Sherif and A. M. Awad, *J. Inorg. Nucl. Chem., 19,* 94 (1961).
14 J. C. Dewan, A. J. Edwards, D. R. Slim, J. E. Guerchais and R. Kergoat, *J. Chem. Soc. Dalton,* 2171 (1975).
15 C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York (1970) p. 47.
16 M. Michlmayr, G. Gritzner and V. Gutmann, *Inorg. Nucl. Chem. Letters, 2,* 227 (1966).
17 T. A. O'Donnel, "Comprehensive Inorganic Chemistry", Pergamon Press, Oxford (1973) vol. 2, p. 1092.
18 J. Heirovsky and J. Kuta, "Principles of Polarography", Academic Press, New York (1966) p. 156.
19 C. Keller, "The Chemistry of Transuranium Elements", Springer Verlag, Berlin (1971).
20 N. Tanaka and T. Murayama, *Z. Phys. Chem. N. F., 11,* 366 (1957).
21 J. I. Briant and M. D. Kemp, *Anal. Chem., 32,* 758 (1960).
22 R. Schrader and G. Pretzschner, *Talanta, 13,* 1105 (1966).
23 R. G. Pearson, *J. Am. Chem. Soc., 85,* 3533 (1963).
24 S. Ahrland and E. Avsar, *Acta Chem. Scand., A30,* 15 (1976).