Polarographic Investigations on Uranyl(VI) Complexes in Dimethylsulfoxide. II. Aliphatic Amines

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The complex formation reaction between some aliphatic amines and uranyl(VI) ion in dimethylsulfoxide has been investigated by polarographic and spectrophotometric methods. Primary amines such as n-butylamine and n-hexylamine give a distinct cathodic wave which may be discussed in term of the successive 1:1, 2:1 and 3:1 amine uranyl(VI) complexes formation. On the contrary tert-butylamine gives two distinct cathodic waves; the first indicates the existence of the stable 1:1 complex, while the second is attributable to the 2:1 and 3:1 amine uranyl(VI) complexes. Secondary straight-chain amines qualitatively behave as primary straight-chain amines. Tertiary amines show a poor coordinating ability for uranium-(VI) and only triethylamine suggests the ultimate formation of the 3:1 complex. The coordinating abilities of the amines studied decrease in the series $NH_2R > NHR_2 > NR_3$.

Introduction

As a part of a systematic study dealing with the complex formation of uranium(VI) with donors of different bonding characteristics in dimethylsulfoxide [1, 2], the present paper investigates the behaviour of aliphatic amines as ligands.

Interactions between metallic ions and aliphatic amines have not extensively been studied until now either in aqueous or in aprotic solvents [3–5], and the study of complex formation of uranium(VI) with amines has been mainly directed to high molecular weight ones, because of their use as selective extracting agents [6].

This paper deals with a polarographic and spectrophotometric study of the complexes formed between uranyl(VI) ion and n-butyl-, n-hexyl, tert- butyl-, di-n-butyl-, triethyl- and tri-n-butylamine in order to investigate both the coordinating ability of primary, secondary and tertiary amines and the possible role of steric and chain-length effects.

Experimental

Chemicals

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

Reagent grade n-butyl-, n-hexyl-, triethyl- and tri-n-butylamine were Carlo Erba products; tert- butyl- and di-n-butylamine were Fluka products.

Apparatus and Methods

The polarographic and coulometric apparatus have been already reported [2].

The spectrophotometric experiments were carried out by using a Perkin–Elmer 124 Spectrophotometer equipped with a Perkin–Elmer 56 Recorder.

The uranyl(VI) solvate $[UO_2(NO_3)_2 \cdot 5DMSO]$ was added as weighed quantity, while amines were added as known volumes from stock solutions by using a micrometer siringe outfit (Burroughs Wellcome Co., London).

A DMSO–0.1M TBAP solution was used as a blank for spectrophotometric measurements.

All experiments were carried out at 25 °C.

Results and Discussion

The voltammetric behaviour of uranyl(VI) ion in DMSO has been previously reported [1].

Spectrophotometric measurements performed on amine solutions revealed low absorption peaks in the u.v. region at about 270 nm; on the contrary uranium(VI) exhibits strong absorption peaks in the u.v. region and two peaks with lower molar absorptivity in the visible [7]. Uranyl(VI)–amine complexes showed absorption peaks in the same regions of uranyl(VI) alone.
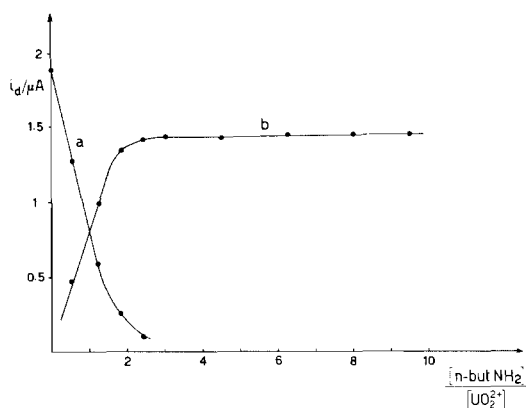
Figure 1. Current trend of the polarographic reduction processes as a function of the mol ratio n-butylamine/UO_2^{2+}. Uranium(VI) concentration: $1.04 \times 10^{-3} M$.
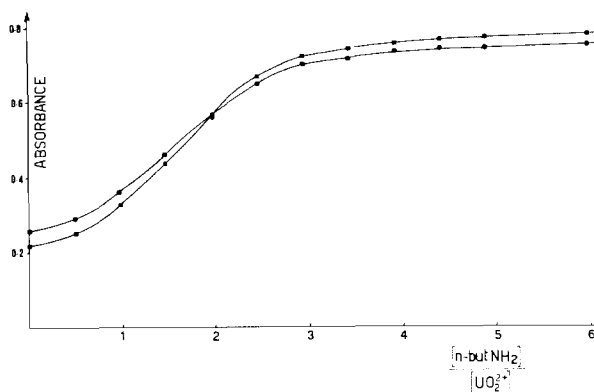

Figure 2. Dependence of the complexes absorbance on the mol ratio n-butylamine/UO_2^{2+}; ● 430 nm; ■ 442 nm; (experimental conditions as in Fig. 1).

For our purpose it would be useful to look into the concentration changes both of the free species [uranyl(VI) ion and amine] and of the complexes. The polarographic technique allows one to follow the uranyl(VI) ion and the relative amine complexes, while the very low molar absorptivity of amines in contrast to the very strong absorption of uranium(VI) prevented reliable measurements in the u.v. region on free amines. Therefore the spectrophotometric measurements have been restricted to the formed complex species in the visible region.

Primary Amines

n-Butylamine

The addition of increasing amounts of n-butylamine to the uranyl solution caused a progressive lowering of the cathodic wave of uranium(VI) ($E_{1/2}$ = −0.53V) and correspondingly a second cathodic process took place. The half-wave potential of the second process initially shifted from −0.85V towards more negative values up to a constant value of −0.98V. Successively a small and poorly defined third cathodic process could be detected. In addition to the cathodic processes an anodic wave appeared ($E_{1/2}$ = +0.13V) due to the formation of stable mercury amine complexes.

In Fig. 1 the trend of the limiting current of the above processes against the mol ratio amine/UO_2^{2+} is plotted.

Logarithmic analysis [E *vs.* log $(i_d − i)/i$] of the wave corresponding to the process "b" gave a straight line with a slope of 0.070V.

Controlled potential coulometric experiments carried out at potential values corresponding to the limiting current of the cathodic process "b" at a mol ratio amine/UO_2^{2+} of about 2/1 gave a n_e-value of 1.1 [1]. These data point out that the above one-electron reduction process can be considered almost reversible.

By considering Fig. 1 it can be noted that the limiting current of the free uranyl(VI) ion reduces to a half and crosses curve "b" just at mol ratio 1/1. In addition curve "b" reaches its maximum value near to the 2/1 mol ratio. These facts strongly suggest the formation of the 2:1 amine–uranyl(VI) complex.

In Fig. 2 the spectrophotometric results, obtained under the same experimental conditions as the polarographic ones, are reported. The trend of the absorbance indicates the ultimate formation of the 3:1 complex.

It is noteworthy that in correspondence to the maximum absorbance value (mol ratio about 3/1) the polarographic data of the process "b" show no shift in $E_{1/2}$ values.

It can be concluded hence that the reduction process "b" is attributable to the successive formation of the three complexes: $UO_2(\text{n-but } NH_2)^{2+}$, $UO_2(\text{n-but } NH_2)_2^{2+}$, $UO_2(\text{n-but } NH_2)_3^{2+}$, characterized by similar stability constant values. The plot of $E_{1/2}$ values against the logarithm of amine concentration was curved and could be interpreted in terms of a sequence of (p − q) values of 2, 1 and 0 respectively [1, 2, 8]. Also these data suggest the successive formation of different uranyl–amine complexes. The (p − q) value of 0 evidentiates the formation of the 3:1 complex both of uranyl(VI) and uranyl(V).

From the difference in $E_{1/2}$ values between the free uranyl(VI) wave (−0.53V) and that of the 3:1 complex (−0.98V) the ratio of the stability constants of the oxidized and reduced forms, β_{Ox}/β_{Red}, can be calculated; it resulted:

$$\frac{\beta_{Ox}}{\beta_{Red}} = 4 \times 10^7$$

where β_{Ox} and β_{Red} both refer to the 3:1 complex.

n-Hexylamine

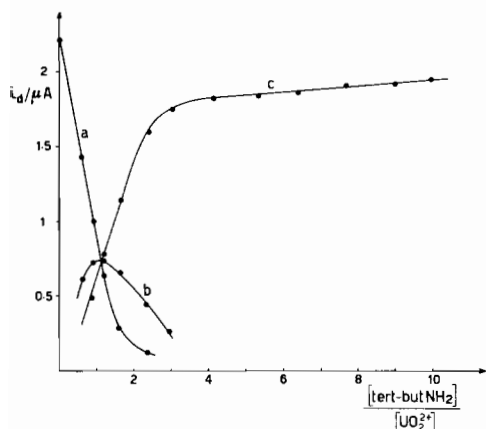The polarographic behaviour exhibited by uranyl-(VI)–n-hexylamine solutions is very similar to that

Figure 3. Current trend of the polarographic reduction processes as a function of the mol ratio tert-butylamine/UO_2^{2+}. Uranium(VI) concentration: 1.23×10^{-3} *M*.

Figure 4. Current trend of the cathodic processes as a function of the mol ratio triethylamine/UO_2^{2+}. Uranium(VI) concentration: 8.82×10^{-4} *M*.

reported above for n-butylamine, giving rise to a current plot analogous to that reported in Fig. 1. The process "b" shifted from -0.85 V towards more negative values at increasing amine additions reaching the constant value of -0.96 V, suggesting also in this case the existence of the 1:1, 2:1 and 3:1 amine–uranyl(VI) complexes.

The ratio of the stability constants for the 3:1 complex was found to be:

$$\frac{\beta_{Ox}}{\beta_{Red}} = 2 \times 10^7$$

tert-Butylamine

Uranium(VI) solutions containing increasing amounts of tert-butylamine gave a polarographic picture somewhat different from those described above, in that the wave of free uranium(VI) more steeply decreases as a second reduction process takes place, followed in turn by a well defined third one. The $E_{1/2}$ of the second cathodic process was constant at -0.77 V, while the third process initially occurred at a $E_{1/2}$ value of -0.94 V, shifted towards negative values and remained substantially constant at -1.02 V for a mol ratio amine/UO_2^{2+} near to 3/1.

In Fig 3 the dependence of the limiting currents of the observed polarographic processes on the mol ratio amine/UO_2^{2+} is reported. As can be noted the process "c" rapidly replaces the process "b", which exhibits a sharp maximum at the 1/1 mol ratio; this suggests that the species involved in the process "c" are more stable at relatively high amine concentrations.

Logarithmic analysis of waves "b" and "c" revealed an almost reversible behaviour for both processes.

At mol ratios greater than 2/1 the change in $E_{1/2}$ values of waves "c" as a function of the logarithm of amine concentration indicated a (p − q) value of about 1.
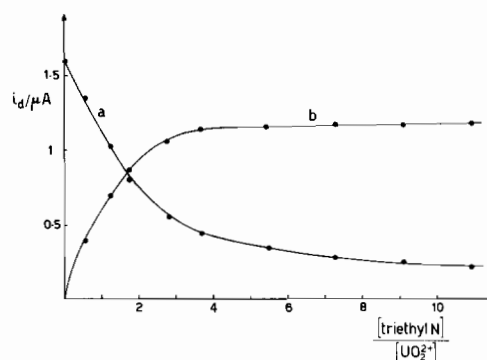
The spectrophotometric measurements resulted quite similar to those reported in Fig. 2, clearly indicating also in this case the ultimate formation of the 3:1 complex. In this connection the polarographic results can be discussed as follows: the process "b" indicates the existence of the 1:1 amine–uranyl(VI) complex, followed by the successive process "c" which indicates the formation of both 2:1 and 3:1 complexes.

Taking into account the data relative to the cathodic processes where no $E_{1/2}$ shift occurs, it is possible to calculate two stability constants ratios:

$$\frac{\beta_{Ox}}{\beta_{Red}} = 1 \times 10^4$$

where β_{Ox} and β_{Red} both refer to the 1:1 complex, and:

$$\frac{\beta_{Ox}}{\beta_{Red}} = 2 \times 10^8$$

where β_{Ox} and β_{Red} refer now to the 3:1 complex.

Secondary Amines

Di-n-butylamine

The polarographic and spectrophotometric behaviour exhibited by uranyl(VI) solutions containing increasing amounts of di-n-butylamine was qualitatively very similar to that exhibited by n-butylamine solutions. Also in this case at mol rato higher than 3/1 the $E_{1/2}$ value of wave "b" remained practically constant at -0.92V. Hence again we suppose that the process "b" is attributable to the formation of successive 1:1, 2:1 and 3:1 complexes.

The ratio of stability constants for the 3:1 complex resulted:

$$\frac{\beta_{Ox}}{\beta_{Red}} = 4 \times 10^6$$

TABLE I. Stability Constant Ratios of 3:1 Amine–Uranyl(VI) Complexes in DMSO.

	n-Butylamine	n-Hexylamine	tert-Butylamine	Di-n-butylamine	Triethylamine
$\dfrac{\beta_{Ox}}{\beta_{Red}}$	4×10^7	2×10^7	2×10^8	4×10^6	4×10^5

Tertiary Amines

Triethylamine

The addition of increasing amounts of triethylamine to the uranyl(VI) solution produced a lowering of uranium(VI) limiting current slower than that observed in the case of primary and secondary amines (Fig. 4). As can be observed the process "b" slowly reaches its maximum value at ratios of about 4/1, where the $E_{1/2}$ remains constant ($E_{1/2} = -0.86$ V). At lower ratios a $(p - q)$ value of 1 was found. The spectrophotometric results confirmed the weaker complexation of uranium(VI) and the probable ultimate formation of the 3:1 complex.

From $E_{1/2}$ values we calculated a β_{Ox}/β_{Red} ratio of 4×10^5 for the 3:1 complex.

Tri-n-butylamine

The polarographic picture given by additions of tri-n-butylamine to the uranyl(VI) solution was qualitatively similar to that discussed above for triethylamine, but the complexation was even weaker, as suggested by the presence of wave "a" which is higher than wave "b" also at mol ratios of the order of 20/1. The half-wave potential of wave "b" occurred at −0.75 V.

Conclusions

The above results indicate that stable complexes form between uranium(VI) and the investigated amines in DMSO in contrast with what occurs in aqueous media, where amine complexes with type "a" or "hard" acceptors such as the f-block elements cannot form since the oxygen atom of water is a harder donor than the amine nitrogen.

The results also indicate that under our experimental conditions the maximum number of amine ligands linked to uranyl(VI) ion is three in DMSO and that uranium(VI) forms much stronger amine complexes than uranium(V) [9].

Furthermore the obtained data allow us to correlate the relative stabilities of the studied complexes. In Table I the β_{Ox}/β_{Red} values relative to the 3:1 amine ligand/uranium(VI) complex are summarized; from it, in agreement with literature data [3, 4] it can be deduced that the coordinating ability of amines for uranyl(VI) ion follows the decreasing sequence $NH_2R > NHR_2 > NR_3$, since the stability constants ratios decrease tenfold ranging from n-butyl to di-n-butyl and from di-n-butyl to triethylamine, the ratio for tributylamine being even lower.

Furthermore the chain-length of alkyl group seems to play a slight unfavorable role in the complex formation as shown by the decrease in β values from n-butyl to n-hexylamine and from triethyl to tributylamine. Tert-butylamine exhibits a surprisingly high constant ratio, which could be explained on the basis of the higher basicity of this primary amino group due to the electron donor effect of tert-butyl group; evidently the electron donor effect overcomes the steric effect of the tertiary group. In our opinion these contrasting effects are also responsible for the existence of the distinct 1:1 complex separated from the two successive ones.

Acknowledgements

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