Monatshefte für Chemie 106, 1081—1084 (1975)

Electrometric Study of Uranyl(II) and Beryllium(II) Complexes of 2,2′-Dimercapto Diethyl Ether

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With 2 Figures

(Received March 14, 1975)

Complexation of uranyl(II) and beryllium(II) ions with 2,2′-dimercaptodiethyl ether has been studied in 40% ethanolic media by potentiometric and conductometric titration techniques revealing the formation of an 1 : 1 complex in either case. The stability constants of the complexes have been determined at ionic strength $\mu = 0.1M$ ($NaClO_4$) by applying *Calvin* and *Melchior's* extension of *Bjerrum's* method. Log K_{stab} values are found to be 12.60, 11.96 at 25 °C and 12.55, 11.90 at 35 °C respectively. The values of ΔG, ΔH and ΔS for the complexation reactions determined at 25 °C are also reported.

Introduction

Metal complexes of several mercapto compounds have been studied by *Saxena* and coworkers[1–5]. This paper reports the determination of composition and stabilities of uranyl and beryllium complexes of 2,2′-dimercapto diethyl ether at 25 and 35 °C by applying potentiometric and conductometric titration techniques and also the values of ΔG, ΔH and ΔS at 25 °C accompanying the complexation reactions. There is, however, no reference in the literature on the study of the present systems.

Experimental

2,2′-dimercapto diethyl ether [referred herein as $R(SH)_2$] was obtained from Evan's Chemetics Inc. (New York), and other chemicals used were of Anal-R (BDH) grade. The studies were carried out in 40% ethanolic media and the ionic strength of the solution was maintained by $NaClO_4$.

A Cambridge Bench pH meter and electronic eye type conductometer were used for potentiometric and conductometric titrations. The Universal thermostat U_3 type (Germany) was used to maintain the desired temperature. The stability constants of the complexes were determined from the titration curves of the following solutions adopting *Calvin* and *Melchior's* extension of *Bjerrum's* method.

A. 12.0 mM $R(SH)_2$ + 0.1 M $NaClO_4$ + 4.2 mM $HClO_4$ + 40% ethanol;

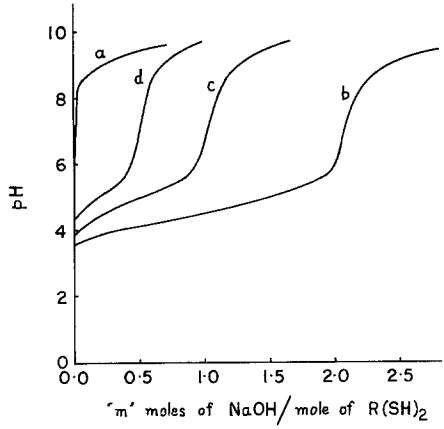

Fig. 1. Potentiometric titration curves of the solutions. *a* 4.0 mM $R(SH_2)$, *b* 4.0 mM $R(SH)_2$ + 4.0 mM UO_2^{2+}, *c* 4.0 mM $R(SH)_2$ + 2.0 mM UO_2^{2+} and *d* 4.0 mM $R(SH_2)$ + 1.0 mM UO_2^{2+} against 0.1 M NaOH

B. 12.0 mM $R(SH)_2$ + 2.0 mM metal ion (UO_2^{2+} or Be^{2+}) + 0.1 M $NaClO_4$ + 4.2 mM $HClO_4$ + 40% ethanol against 0.1 M NaOH at 25 and 35 °C.

Results and Discussion

Stoichiometry

The stoichiometry of the complexes formed between metal ions and the ligand was established by titrating the solutions containing different moles of $R(SH)_2$ per mole of metal ion against standard NaOH. Fig. 1 shows the pH titration curves of (a) 4.0 mM $R(SH_2)$, (b) 4.0 mM $R(SH)_2$ + 4.0 mM UO_2^{2+}, (c) 4.0 mM $R(SH)_2$ + 2.0 mM UO_2^{2+} and (d) 4.0 mM $R(SH)_2$ + 1.0 mM UO_2^{2+} against 0.1*M*-NaOH. The abscissa '*m*' denotes the moles of NaOH per mole of $R(SH)_2$.

Curve (a) indicates that the protons of the SH groups are not titrable under the experimental conditions. The addition of equimolar concentration of metal ion alters the shape of the curve showing the com-

plex formation between metal ion and hence the lowering of buffer region. The inflexion at $m = 2.0$ (curve b) shows the formation of 1 : 1 complex as explained by the equation:

$$R(SH)_2 + UO_2^{2+} + 2\,OH^- \rightleftharpoons UO_2(RS_2) + 2\,H_2O. \quad (1)$$

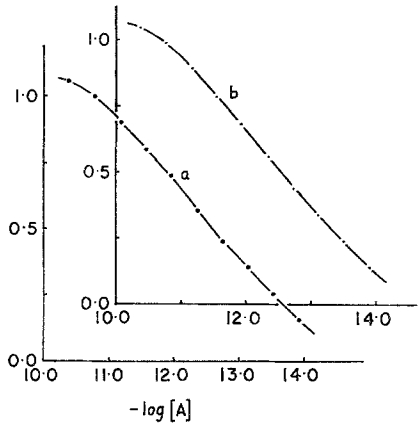

Fig. 2. Formation curves for uranyl complexes at *a* 25 °C and *b* 35 °C

When metal and ligand were mixed in the ratio 1 : 2 and 1 : 4 the inflections were obtained at $m = 1.0$ and 0.5 resp. confirming the formation of 1 : 1 complex as given below:

$$2\,R(SH)_2 + UO_2^{2+} + 2\,OH^- \rightleftharpoons UO_2(RS_2) + R(SH)_2 + 2\,H_2O \quad (2)$$

and

$$4\,R(SH)_2 + UO_2^{2+} + 2\,OH^- \rightleftharpoons UO_2(RS_2) + 3\,R(SH)_2 + 2\,H_2O. \quad (3)$$

Similar curves were obtained for Be^{2+} complexes indicating the formation of 1 : 1 complex.

Conductometric Titrations

Conductometric titrations of the solutions containing metal ions and the ligand mixed in different ratios were also performed against standard NaOH and the titration curves revealed the formation of 1 : 1 complex in both the cases as obtained from pH titration curves.

Stability Constants

The stability constants of the above complexes have been determined at 25 and 35 °C by applying *Bjerrum's* method[6] as extended by *Calvin* and *Melchior*[7]. The solutions of $R(SH)_2$ in absence and pres-

ence of metal ions were titrated with NaOH from which the values of formation function, $\bar{n}$ and the free ligand concentration, $[A]$ were calculated. The values of $\log K_{stab}$ were then obtained from the formation curves (Fig. 2) at $\bar{n} = 0.5$ and found to be 12.60, 11.96 at 25 °C and 12.55, 11.90 at 35 °C for uranyl and beryllium complexes respectively.

Thermodynamic Functions

From the variation of stability constants of the complexes with temperature, the values of change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying the complexation reactions have been determined at 25 °C by applying the standard equations[8] and found to be — 17.30 kcal/mole, — 2.10 kcal/mole and 51.0 cal/mole deg. for UO_2-system and — 16.42 kcal/mole, — 2.52 kcal/mole and 43.29 cal/mole degree for Be-system respectively.

Acknowledgement

The authors thank U.G.C., New Delhi for the grant of a research fellowship to one of them (*S.S.S.*) and the Principal for providing research facilities.

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