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

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With 2 Figures

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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 \( K_{\text{stab}} \) values are found to be 12.60, 11.96 at 25 °C and 12.55, 11.90 at 35 °C respectively. The values of \( \Delta G \), \( \Delta H \) and \( \Delta S \) 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 \( \Delta G \), \( \Delta H \) and \( \Delta S \) 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 U3 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 NaClO₄ + 4.2 mM HClO₄ + 40% ethanol;

![Fig. 1. Potentiometric titration curves of the solutions.](image)

B. 12.0 mM R(SH)₂ + 2.0 mM metal ion (UO₂²⁺ or Be²⁺) + 0.1 M NaClO₄ + 4.2 mM HClO₄ + 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 UO₂²⁺, (c) 4.0 mM R(SH)₂ + 2.0 mM UO₂²⁺ and (d) 4.0 mM R(SH)₂ + 1.0 mM UO₂³⁺ against 0.1M 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-