

Electrometric Study of Uranyl and Thorium Complexes of Ethane 1, 2 Dithiol

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Complex formation of Uranyl (UO_2^{2+}) and Thorium (Th^{4+}) ions with ethane 1, 2 dithiol has been studied in 25% ethanol by potentiometric and conductometric titration techniques. Uranyl ion forms 1:1 complex whose $\log K_{\text{stab}}$ is 13.0 at 25° and 12.35 at 35°. Thorium ion forms two complexes, 1:1 and 1:2 with considerable overlapping and their $\log K_{\text{stab}}$ values are 15.55, 15.09 at 25° and 15.48, 14.96 at 35° respectively. The overall changes in thermodynamic functions ΔG , ΔH , ΔS accompanying complexation, are determined at 35° and are -18.11 Kcal/mole, -6.29 Kcal/mole, 38.37 Cal/deg. for Uranyl complex and -54.02 Kcal/mole, -8.42 Kcal/mole, 115.5 Cal/deg. for Thorium complexes respectively.

SAXENA and co-workers¹⁻⁵ have carried out extensive studies on the complexation of thiols with several metals. This communication deals with the study on complexation of ethane 1, 2 dithiol with uranyl and thorium ions. The composition of these complexes has been determined by potentiometric and conductometric titration techniques and their stability constants are calculated by applying Calvin and Melchior's extension of Bjerrum's method which are further refined by alternative methods such as correction term method and method of solving the equations derived

from $\sum_{n=0}^N (\bar{n}-n) [A]^{n\beta_n} = 0$. The overall changes in

thermodynamic functions ΔG , ΔH , ΔS , accompanying the complexation reactions have been determined at 35°. There is, however, no reference in the literature on the present investigations.

Experimental

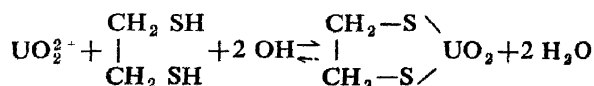
Ethane 1, 2 dithiol and all other chemicals used were of Anala-R (BDH) quality. Freshly prepared solutions were used to avoid any effects of ageing and hydrolysis. pH values were measured on a Cambridge Bench pattern (null deflection) type pH meter associated with glass-calomel electrode assembly. The pH meter was calibrated with the standard buffer solution before and after each series of measurements. The conductance was measured by an electronic eye-type conductometer. A universal thermostat U_3 type (German) was used to maintain the desired temperature. 25% ethanol concentration was maintained throughout the investigation.

The experimental procedure, described earlier,¹⁻⁵ involved a series of pH and conductometric titrations of Ethane 1, 2 dithiol (referred to herein as EDT) in the absence or presence of various proportions of metal ion, against standard NaOH.

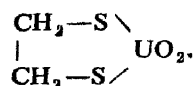
Results and Discussion

Stoichiometry: The stoichiometry of the reactions of the uranyl ion and thorium ion with Ethane 1, 2 dithiol has been determined by potentiometric and conductometric titrations.

The sudden rise in the pH on the addition of NaOH to the free ligand indicates that protons of the -SH groups are not titrable under the experimental conditions (Fig. 1, curve 1). The addition of an equimolar concentration of uranyl ion greatly alters the free ligand titration curve because of complex formation. The fall in the initial pH value clearly shows the displacement of the proton on complexation. Since the extent of the proton displacement depends on the relative affinity of ligand for hydrogen ion and the metal ion, it is obvious from the curve that the interaction of UO_2^{2+} ion with EDT is sufficient for it to compete with a relatively high concentration of hydrogen ions and hence there is considerable lowering of buffer region. The appearance of a precipitate and an inflection at $m=2$ (Fig. 1, curve 4) suggests the formation of 1:1 complex in accordance with the following equation:



The titration curves of a solution containing UO_2^{2+} and ligand in the ratio 1:2 and 1:4 offer additional information about complexation process. They give inflections at $m=1$ and $m=0.5$ respectively (Fig. 1, curves 2, 3) which corresponds to the formation of



*m represents moles of NaOH added per mole of ligand.

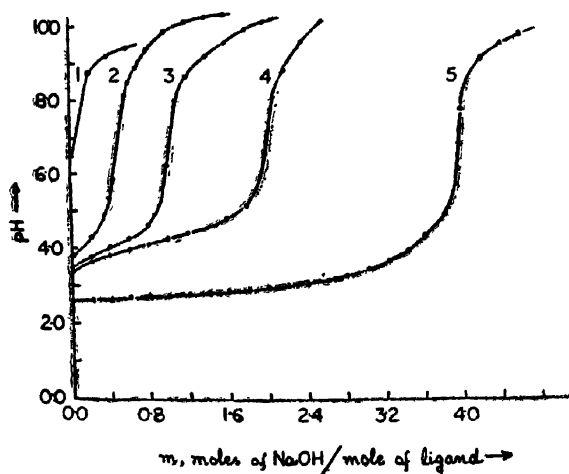
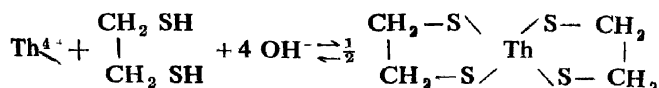


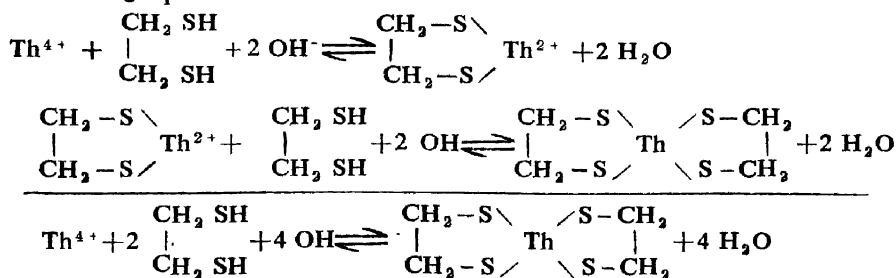
Fig. 1: Potentiometric titrations of EDT in absence and presence of UO_2^{2+} and Th^{4+} with $0.1 M NaOH$.

Curve 1 = $4 \times 10^{-3} M EDT$, Curve 2 = $4 \times 10^{-3} M EDT + 1 \times 10^{-3} M UO_2^{2+}$, Curve 3 = $4 \times 10^{-3} M EDT + 2 \times 10^{-3} M UO_2^{2+}$, Curve 4 = $4 \times 10^{-3} M EDT + 4 \times 10^{-3} M UO_2^{2+}$, Curve 5 = $4 \times 10^{-3} M EDT + 4 \times 10^{-3} M Th^{4+}$.

Similarly there is fall in the initial pH value of the ligand solution with the addition of an equimolar concentration of Th^{4+} ions showing the complex formation. The appearance of a precipitate and an inflection at $m=4$ (Fig. 1, curve 5) suggests the formation of 1 : 2 complex according to the following equation :



An inflection at $m=2$ when Th^{4+} and ligand are in the ratio of 1 : 2 also indicates the formation of 1 : 2 complex. Since there is no significant inflection at $m=1$ (when the ratio is 1 : 2), the formation of 1 : 1 and 1 : 2 complexes must overlap considerably in accordance with the following equations :



i. e. 1 : 1 and 1 : 2 complexes are being formed simultaneously. The inflection at $m=1$ when the ratio of metal to ligand is 1 : 4, confirms this conclusion.

The conductometric titration of the free ligand with standard NaOH shows a rapid increase in conductance from the starting point indicating the failure of the -SH groups to dissociate, the change in conductance being merely due to the additional NaOH (Fig. 2, curve 1). When the ratio of EDT to UO_2^{2+} ion in the solution is 1 : 1, 2 : 1 and 4 : 1, the breaks in

the conductance curves were observed at $m=2$, $m=1$ and $m=0.5$ respectively which reveal the formation of 1 : 1 complex. In the case of Th^{4+} and EDT solutions mixed in the ratio 1 : 1, the breaks at $m=2$ and $m=4$ (Fig. 2, curve 3) correspond to the formation of 1 : 1 and 1 : 2 complexes which were further confirmed from the titration curves of the solutions containing the

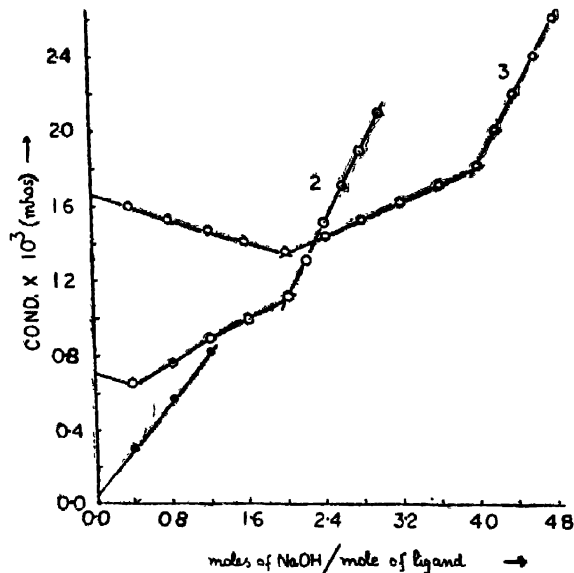
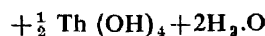


Fig. 2: Conductometric titrations of EDT in absence and presence of UO_2^{2+} and Th^{4+} with $0.1 M NaOH$.

Curve 1 = $4.0 \times 10^{-3} M EDT$, Curve 2 = $4 \times 10^{-3} M EDT + 4 \times 10^{-3} M UO_2^{2+}$, Curve 3 = $4 \times 10^{-3} M EDT + 4 \times 10^{-3} M Th^{4+}$.



metal and the ligand in the ratio 1 : 2 and 1 : 4. These results are similar to those obtained by pH titrations.

Stability Constants : The stability constants of complexes have been calculated adopting Bjerrum's method⁶ as extended by Calvin and Melchior⁷. A

series of pH titrations of EDT in $0.1 M NaClO_4$ and $0.005 M HClO_4$ were carried out in absence and presence of the metal ion at two different temperatures. The horizontal distance between the resulting curves was used to calculate the concentration of the bound ligand which was divided by the total metal ion concentration to give the formation function \bar{n} . Concentrations of the free ligand [A] at various pH

values have been calculated from the relation

$$[A] = \frac{\text{total ligand} - \text{ligand bound}}{\frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_1} + 1}$$

where K_1 and K_2 are the dissociation constants of the two -SH groups in EDT; the values of which, determined by Cheney method⁸, are 3.96×10^{-10} and 2.44×10^{-11} respectively. Formation curves at two different temperatures were obtained by plotting \bar{n} vs-log [A] (Fig. 3).

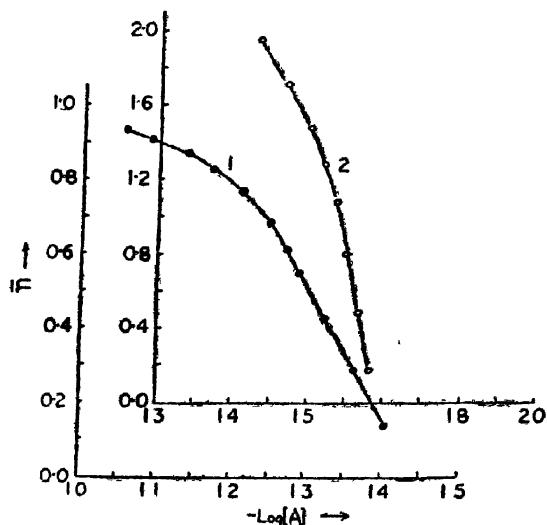


Fig. 3: Formation curves at 25° : (1) EDT : UO₂²⁺ system, (2) EDT : Th⁴⁺ system.

$$K_1 = \frac{1}{[A]} \frac{\bar{n}}{(1-\bar{n}) + (2-\bar{n}) K_2 [A]}$$

and

$$K_2 = \frac{1}{[A]} \frac{\bar{n} + (\bar{n}-1) K_1 [A]}{(2-\bar{n}) K_1 [A]}$$

The values of log K_1 and log K_2 are summarised in Table 1.

Thermodynamic functions : The values of overall changes in free energy (ΔG), enthalpy (ΔH) and Entropy (ΔS), accompanying complexation, have been determined at 35° with the help of standard equations¹⁰. The stability constant of the complex of the type MA_n ($M+nA \rightleftharpoons MA_n$) is related to the free energy changes (ΔG) by the following equation :

$$\Delta G = -RT \ln K_{stab}$$

ΔH is determined with the help of isobar

$$\text{equation : } \frac{d \ln K_{stab}}{dT} = \frac{\Delta H}{RT^2}$$

ΔS is related to ΔG and ΔH by the equation $\Delta S = (\Delta H - \Delta G)/T$

For UO_2^{2+} : EDT system the values of ΔG , ΔH and ΔS are found to be -18.11 Kcal/mole, -6.29 Kcal/mole and 38.37 Cal/deg respectively. While for Th^{4+} : EDT system the respective values of these functions are -54.02 Kcal/mole, -8.42 Kcal/mole and 115.5 Cal/deg.

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TABLE I—VALUES OF LOG K_{stab} OF THORIUM : EDT COMPLEXES.

S. No.	Methods.	Temp. 25°			Temp. 35°		
		log K_1	log K_2	log β	log K_1	log K_2	log β
1.	Calvin and Melchior's extension of Bjerrum's method.	15.65	14.97	30.62	15.57	14.85	30.42
2.	Correction term method.	15.57	15.11	30.68	15.49	14.99	30.48
3.	Method of solving simultaneous equations.	15.44	15.18	30.62	15.27	15.05	30.42
	Mean	15.55	15.09	30.64	15.48	14.96	30.44

As for UO_2^{2+} : EDT system the maximum value of \bar{n} is not greater than 1, only 1 : 1 complex is formed. The values of log K_{stab} at 25° and 35° are read directly from the formation curves at $\bar{n}=0.5$ and are 13.00, 12.35 respectively.

For Th^{4+} : EDT system, the value of $n=2$ shows that the highest complex formed is 1 : 2. The values of log K_1 and log K_2 were determined by finding -log [A] at $\bar{n}=0.5$ and $n=1.5$ respectively. These values were further refined by using the following methods :

- (1) Correction term method⁹.
- (2) Method of solving simultaneous equations derived from Bjerrum's formation function⁶.

$$\sum_{n=0}^N (\bar{n}-n) [A]^n \beta_n = 0$$

For the present case $N=2$.

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