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Stabilities and Thermodynamics of Uranyl(II) and Thorium(IV) Complexes of 2-Mercaptoethanol

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With 3 Figures

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The complexation of UO_2^{+2} and Th^{+4} ions with 2-mercaptoethanol has been studied by potentiometric and conductometric titration techniques. Uranyl ion forms 1 : 1 and 1 : 2 complexes in the pH-range 3.3–6.5 and thorium ion forms 1 : 2, 1 : 3, and 1 : 4 complexes in the pH-range 3.2–4.8 with considerable overlapping. Their log $k_{\text{stab.}}$ values are determined at 10, 20, and 30 °C at ionic strength $\mu = 0.1 M$ ($NaClO_4$) by applying *Calvin-Melchior's* extension of the *Bjerrum* method. The overall changes in thermodynamic functions ΔG, ΔH, and ΔS accompanying complexation determined at 20 °C are — 19.48 kcal/mole, — 22.77 kcal/mole, — 11.23 cal/deg · · mole for uranyl complexes and — 33.94 kcal/mole, — 4.93 kcal/mole, 99.00 kcal/deg · mole for thorium complexes, resp.

Introduction

Thiols, containing an active SH group have a wide range of applications in biological, pharmaceutical, industrial and other chemical fields and are well known for their tendency to form complexes with metals. Several metal complexes of thiols have already been studied by *Saxena* et al.[1–4]. The present communication reports the composition and stabilities of 2-mercaptoethanol complexes of uranyl (UO_2^{+2}) and thorium (Th^{+4}) ions and the overall changes in free energy, enthalpy, entropy accompanying their complexation reactions.

Experimental

2-mercaptoethanol (referred herein as RSH) was obtained from B.D.H., Poole, England, and all the other chemicals were of Anala-R (B.D.H.) grade. pH-measurements were made on a Cambridge bench pattern (null deflection type) pH-meter associated with glass calomel electrode assembly. Conductance was measured on an electronic eye-type conductometer. A universal thermostat U_3 type (German) was used to maintain the desired temperature. The experimental procedure as described earlier[2], involved a series of pH and conductometric titrations of RSH in absence and presence of different ratios of metal ion to ligand against standard NaOH.

Results and Discussion

Stoichiometry

For establishing the stoichiometry of the complex species formed during the interaction of metal ion and RSH, the magnitude of proton displacement was determined by titrating the solution containing metal ion and RSH in different molar ratios viz. 1 : 1, 1 : 2, 1 : 3, 1 : 4 against standard NaOH.

On the addition of NaOH to the ligand, a sudden rise in pH was observed (Fig. 1, curve 1) indicating the non-titrability of the proton of SH group under experimental conditions. The addition of an equimolar concentration of metal ion greatly alters the shape of the free ligand titration curve (Fig. 1, curve 5) indicating the complex formation which results in the lowering of buffer region due to the proton displacement.

$$M^{+n} + \mathrm{RSH} \rightleftharpoons M(\mathrm{RS})^{+(n-1)} + \mathrm{H}^+$$

where M^{+n} stands for UO_2^{+2} and Th^{+4}.

Since the extent of proton displacement depends on the relative affinity of ligand for H^+ and the metal ion, it is obvious from the curve that the interaction of M^{+n} ion with RSH is sufficient to compete with a relatively high concentration of hydrogen ions.

For UO_2^{+2}: The appearance of precipitate and an inflection in the vicinity of $m = 2$ (m being the moles of NaOH per mole of RSH) suggests the formation of $UO_2(RS)_2$ and $UO_2(OH)_2$ in accordance with the following equation[5]:

$$\mathrm{UO_2^{+2} + RSH + 2\,OH^- \rightleftharpoons \tfrac{1}{2}\,UO_2(RS)_2 + \tfrac{1}{2}\,UO_2(OH)_2 + HOH}$$

An inflection at $m = 1$ when metal ion and ligand in the ratio of 1 : 2 corresponds to the formation of $UO_2(RS)_2$. Since there is no significant inflection at $m = 0.5$, the formation of $UO_2(RS)^+$ and $UO_2(RS)_2$ must overlap considerably in accordance with the following equations:

$$\begin{array}{l}
\mathrm{UO_2^{+2} + RSH + OH^- \rightleftharpoons UO_2(RS)^+ + HOH} \\
\mathrm{UO_2\,(RS)^+ + RSH + OH^- \rightleftharpoons UO_2(RS)_2 + HOH} \\
\hline
\mathrm{UO_2^{+2} + 2\,RSH + 2\,OH^- \rightleftharpoons UO_2(RS)_2 + 2\,HOH}
\end{array}$$

i.e. 1 : 1 and 1 : 2 complexes are formed simultaneously. The inflection at $m \approx 0.67$ when ratio of metal to ligand is 1 : 3, also supports the above conclusion.

For Th^{+4}: The appearance of precipitate and an inflection in the vicinity of $m = 4$, suggest the formation of $Th(RS)_4$ as the highest complex and $Th(OH)_4$ in accordance with the following equation

$$Th^{+4} + RSH + 4\,OH^- \rightleftharpoons \tfrac{1}{4}\,Th(RS)_4 + \tfrac{3}{4}\,Th(OH)_4 + HOH$$

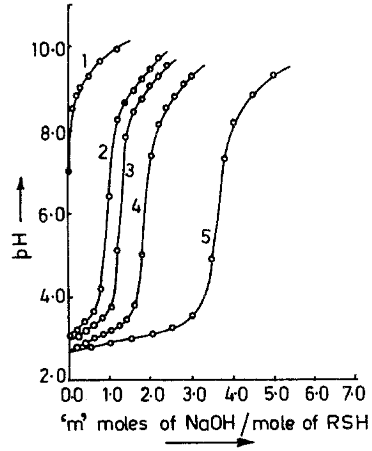

Fig. 1. pH titrations of solutions: *1* $4.0 \times 10^{-3}M$-RSH; *2* $4.0 \times 10^{-3}M$-RSH + $1.0 \times 10^{-3}M$-$Th(NO_3)_4$; *3* $4.0 \times 10^{-3}M$-RSH + $1.33 \times 10^{-3}M$-$Th(NO_3)_4$; *4* $4.0 \times 10^{-3}M$-RSH + $2.0 \times 10^{-3}M$-$Th(NO_3)_4$; *5* $4.0 \times 10^{-3}M$-RSH + $4.0 \times 10^{-3}M$-$Th(NO_3)_4$

When metal ion and ligand are mixed in the ratio 1 : 2, 1 : 3, and 1 : 4, the precipitation and inflections are obtained at $m \approx 2.0$, 1.3, and 1.0 resp. (Fig. 1). These inflections suggest the formation of $Th(RS)_2^{+2}$, $Th(RS)_3^{+}$, and $Th(RS)_4$ corresponding to 1 : 2, 1 : 3, and 1 : 4 complexes resp. with considerable overlapping according to the following equations

$$\begin{array}{l} Th^{+4} + 2\,RSH + 2\,OH^- \rightleftharpoons Th(RS)_2^{+2} + 2\,HOH \\ Th(RS)_2^{+2} + RSH + OH^- \rightleftharpoons Th(RS)_3^{+} + HOH \\ Th(RS)_3 + RSH + OH^- \rightleftharpoons Th(RS)_4 + HOH \\ \hline Th^{+4} + 4\,RSH + 4\,OH^- \rightleftharpoons Th(RS)_4 + 4\,HOH \end{array}$$

i.e. 1 : 2, 1 : 3, and 1 : 4 complexes are formed simultaneously. In all the above cases the precipitation of metal hydroxide may be explained as follows:

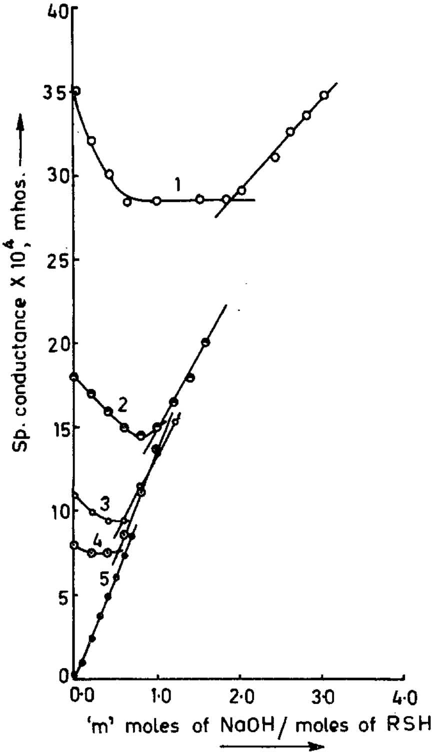

Fig. 2. Conductometric titrations of solutions: *5* $4.0 \times 10^{-3}M$-RSH; *4* $4.0 \times 10^{-3}M$-RSH + $1.0 \times 10^{-3}M$-$UO_2(NO_3)_2$; *3* $4.0 \times 10^{-3}M$-RSH + + $1.33 \times 10^{-3}M$-$UO_2(NO_3)_3$; *2* $4.0 \times 10^{-3}M$-RSH + $2.0 \times 10^{-3}M$-$UO_2(NO_3)_2$; *1* $4.0 \times 10^{-3}M$-RSH + $4.0 \times 10^{-3}M$-$UO_2(NO_3)_2$

For 1 : 2 *complex*

$$Th(RS)_2^{+2} + 2\,OH^- \rightleftharpoons \tfrac{1}{2}\,Th(RS)_4 + \tfrac{1}{2}\,Th(OH)_4$$

For 1 : 3 *complex*

$$Th(RS)_3^{+} + OH^- \rightleftharpoons \tfrac{3}{4}\,Th(RS)_4 + \tfrac{1}{4}\,Th(OH)_4$$

For 1 : 4 *complex*

$$Th^{+4} + RSH + 4\,OH^- \rightleftharpoons \tfrac{1}{4}\,Th(RS)_4 + \tfrac{3}{4}\,Th(OH)_4 + HOH$$

In all cases the appearance of precipitate rules out the possibility of formation of a hydroxo-metal complex[6].

Conductometric titrations of RSH in absence and presence of metal ions mixed in different ratios, against standard NaOH yielded breakes in the curves corresponding to the results obtained from pH-titrations (Fig. 2).

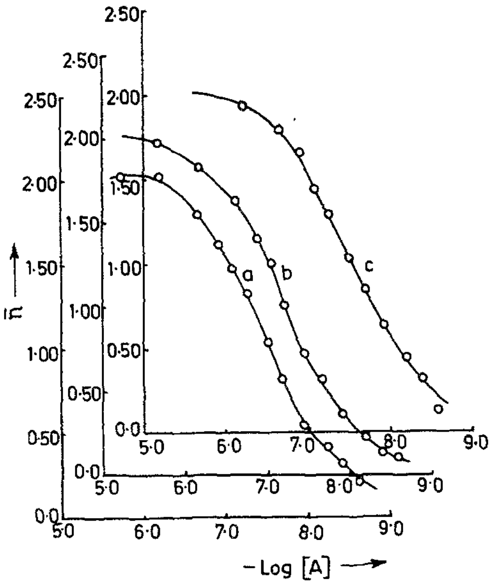

Fig. 3. Formation curves for UO_2^{+2} system at *a* 10 °C, *b* 20 °C, *c* 30 °C

Table 1. *Stability Constants and Thermodynamic Functions for Uranyl(II) and Thorium(IV) Complexes of 2-mercaptoethanol*

Uranyl(II)-complexes			Thorium(IV)-complexes		
Temp., °C	log k_1 (1 : 1)	log k_2 (1 : 2)	log k_2 (1 : 2)	log k_3 (1 : 3)	log k_4 (1 : 4)
10	8.05	7.08	8.62	8.49	8.33
20	7.73	6.80	8.60	8.46	8.25
30	8.08	7.03	8.56	8.41	8.30
Δ *G* (kcal/mole)		— 19.48		— 33.94	
Δ *H* (kcal/mole		— 22.77		— 4.93	
Δ *S* (kcal/deg. mole)		— 11.23		99.00	

Stability Constants

Calvin and *Melchior*'s[7] extension of the *Bjerrum* method[8] has been employed for the determination of stability constants of the complexes. The pH-titrations of RSH solution at ionic strength $\mu = 0.1 M$ ($NaClO_4$) in absence and presence of metal ions carried out at 10, 20, and 30 °C against $0.1 M$-NaOH and the concentration of bound ligand, calculated from the horizontal distance between the corresponding curves, was divided by the total metal ion concentration to obtain formation function ($\bar{n}$). At any pH, the value of free ligand concentration $[A]$, was calculated from the relation

$$[A] = \frac{[\mathrm{RSH}]_{\mathrm{Total}} - [\mathrm{RSH}]_{\mathrm{bound}}}{\mathrm{H}^+/k_a + 1}$$

where k_a is the dissociation constant of RSH determined polarographically[9] as 31.62×10^{-11}. The formation curves obtained at different temperatures by plotting $\bar{n}$ vs. $-\log [A]$ revealed the formation of 1 : 1, 1 : 2 complexes for $\mathrm{UO_2}^+$ (Fig. 3) and 1 : 2, 1 : 3, and 1 : 4 complexes for Th^{+4} ions resp. (Table 1).

Thermodynamic Functions

The values of overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying the complexation reaction have been determined at 20 °C with the help of standard equations[10] (Table 1).

The value of ΔG is obtained from the expression:

$$\Delta G = -RT \ln \beta.$$

where $\beta = k_1 k_2$ [for uranyl ion(II)] and $k_2 k_3 k_4$ [for Th(IV) ion] is the overall stability constant.

ΔH is determined with the help of an isobar $(\mathrm{d} \ln \beta)/\mathrm{d}\, T = \Delta H / RT^2$. The values of $\log \beta$ obtained at different temperatures are plotted as a function of $1/T$. The gradient of the tangent drawn at the point corresponding to 20 °C is determined and equated to $-\Delta H/4.57$. ΔS is then evaluated from the relation

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

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