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STABILITY AND THERMODYNAMICS IN THE INTERACTION OF THIOGLYCOLIC ACID COMPLEXES WITH Y^{3+}, La^{3+}, Be^{2+} AND UO_2^{2+}

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ABSTRACT

Stepwise stability constants of the complexes of thioglycolic acid with Y^{3+}, La^{3+}, Be^{2+} and UO_2^{2+} have been determined by the potentiometric technique of Irving and Rossotti in aqueous solution at 25, 35 and 45 °C, respectively ($\mu = 0.065$ M). The stability of Y^{3+} and La^{3+} complexes increases whereas it decreases with the increase in temperature in the case of Be^{2+} and UO_2^{2+} complexes. The values of enthalpy changes (ΔH) are positive in the case of Y^{3+} and La^{3+} and negative in the case of Be^{2+} and UO_2^{2+}. The complexes of Y^{3+}, La^{3+} and UO_2^{2+} are entropy stabilized. It has been observed that stabilities vary directly with the increase in the ionic strength of the medium in the case of La^{3+}, Be^{2+} and UO_2^{2+} complexes.

INTRODUCTION

The sulphydryl compounds are efficient inhibitors for many enzymes. Thioglycolic acid contains both –COOH and –SH groups. Its chelating behaviour with different metal ions has been reported in the literature by various workers[1–5] whereby it has been recommended as a colorimetric reagent for the determination of various metal ions. However, very little work has been reported on the titration studies involving pH measurements for the determination of stepwise stability constants and thermodynamic parameters of thioglycolic acid complexes. Sarin and Munshi[6] reported the determination of stepwise stability constants and some thermodynamic functions of In(III) complexes with thioglycolic acid. The knowledge of affinity of thioglycolic acid towards metal ions may lead to a better understanding of the enzyme mechanism as thioglycolic acid is a potential ligand containing –COOH and –SH groups which are generally involved in enzyme mechanism. Thus the present work describes the determination of stepwise proton–ligand and metal–ligand stability constants of thioglycolic acid with Y^{3+}, La^{3+}, Be^{2+} and UO_2^{2+} at 25, 35, 45°C and at ionic strengths of 0.065, 0.15 and 0.25 M, respectively. The Bjerrum–Calvin[7–8] pH titration technique as used by Irving and Rossotti[9] has been employed for these investigations. The values of free energies of formation (ΔG), enthalpy changes (ΔH)

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and entropy changes (ΔS) associated with the complexation reaction have been evaluated by the temperature coefficient equations.

EXPERIMENTAL

Materials

All chemicals employed were of reagent grade. Thioglycolic acid was obtained from E. Merck Lab., Germany. The solutions containing the metal were prepared from their respective reagent grade nitrates. The carbonate-free solution of sodium hydroxide was prepared by standard technique using Analar material. Stock solutions of sodium perchlorate (neutral) and perchloric acid were prepared by dissolving Analar (Riedel) $NaClO_4 \cdot H_2O$ and Analar $HClO_4$ (E. Merck) in twice-distilled water.

The stock solution of thioglycolic acid (0.1 M) was standardised against sodium hydroxide potentiometrically. Sodium hydroxide (0.1 M) was also standardised potentiometrically with standard potassium hydrogen phthalate solution. The concentration of perchloric acid (0.05 M) stock solution was also confirmed by potentiometric titration against sodium hydroxide.

Procedure

The following mixtures for the potentiometric titrations were prepared: mixture A: perchloric acid (0.05 M); mixture B: perchloric acid (0.05 M)+thioglycolic acid (0.1 M); mixture C: perchloric acid (0.05 M)+thioglycolic acid (0.1 M)+metal solution.

The ionic strengths of the solutions were adjusted using an appropriate amount of neutral sodium perchlorate solution (1 M) as supporting electrolyte. The final volume was adjusted to 20 ml using twice-distilled water. The titrations were run in duplicate taking a (10:1) ratio of the ligand to metal ion. The titrations were carried out in a nitrogen atmosphere at different temperatures with the titration cell immersed in a thermostatic bath (±0.1 °C). A "Systronix" pH meter with a glass and calomel electrode assembly was used for pH measurements.

The graphs between pH and the volume of alkali were required to be able to plot the corresponding pH changes. The shapes of the titration curves were as usual.

RESULTS AND DISCUSSION

The protonation constants and stability constants were calculated on the basis of formation function applying various computational methods[10]. The calculated values of proton–ligand stability constants of the ligand and the successive stability constants (log K_n) of the various systems at different temperatures and different ionic strengths are given in Tables 1 and 2, respectively. The error limits are ±0.05 for log K_n values. The formation curves of thioglycolic acid complexes with different metal ions for various systems are shown in Figs. 1 and 2. From a perusal of formation curves it is seen that $\bar{n}$ values lie between 0 and 2 in all cases. The titration studies

TABLE 1

STEPWISE PROTONATION CONSTANTS OF THIOGLYCOLIC ACID AT DIFFERENT TEMPERATURES AND IONIC STRENGTHS

T (°C)	*Ionic strength*	*Constants*	
		log K_1^H	*log* K_2^H
25	0.065	10.05	3.67
35	0.065	9.91	3.72
	0.15	9.72	3.54
	0.25	9.58	3.45
45	0.065	9.78	3.80

TABLE 2

STABILITY CONSTANTS OF METAL–THIOGLYCOLIC ACID COMPLEXES AT DIFFERENT TEMPERATURES AND DIFFERENT IONIC STRENGTHS

Metal ion	*Constants*	$\mu = 0.065$			$\mu = 0.15$	$\mu = 0.25$
		$T = 25°C$	$T = 35°C$	$T = 45°C$	$T = 35°C$	$T = 35°C$
Y^{3+}	log K_1	5.28	5.22	5.15	4.95	5.00
	log K_2	3.57	4.80	5.00	4.75	4.89
	log β_2	8.85	10.02	10.15	9.70	9.89
La^{3+}	log K_1	3.65	4.40	4.67	4.57	4.83
	log K_2	3.20	3.24	3.75	3.66	3.88
	log β_2	6.85	7.64	8.42	8.23	8.71
Be^{2+}	log K_1	7.17	6.95	6.82	7.06	7.35
	log K_2	5.41	4.89	4.86	5.00	5.82
	log β_2	12.58	11.84	11.68	12.06	13.17
UO_2^{2+}	log K_1	7.45	7.56	7.40	7.70	7.90
	log K_2	6.58	6.41	6.23	6.45	6.51
	log β_2	14.03	13.97	13.63	14.15	14.41

indicate that complexation starts from pH 5.4, 6, 4.5, 4.0 in the case of Y^{3+}, La^{3+}, Be^{2+} and UO_2^{2+}, respectively. The values of $\bar{n}$ did not exceed 2 in the case of Y^{3+} and La^{3+} due to onset of precipitation at higher pH values. The titration curves of solution in the presence of metals showed significant separation from the corresponding curves in which metal ions were absent.

In the case of Be^{2+} and UO_2^{2+} complexes, even at pH ~4, $\bar{n}$ was already 0.5 showing a strong tendency for complexation and liberation of the proton from the carboxylic group. Thus it is suggested that the ligand forms complexes of 1:2 composition with Y^{3+}, La^{3+}, Be^{2+} and UO_2^{2+}, respectively, in all systems. It is evident from the data (Table 2) that log K_1/K_2 values are always positive for thioglycolic acid complexes.

Comparing the log β_2 values reported in Table 2, for the complexes of Y^{3+} and La^{3+}, it is evident that the stabilities of the Y^{3+} complexes are higher than those of the La^{3+} complexes at all ionic strengths and temperatures. This observed stability order $Y^{3+} > La^{3+}$ is inversely proportional to their decreasing basicities and sizes. It thus suggests that with increasing covalent nature of the metal–ligand bond, the stability increases.

Comparing log β_2 values for Be^{2+} and UO_2^{2+} complexes, it is seen that the observed order is $UO_2^{2+} > Be^{2+}$. This order is in accordance with their Z^2/r values.

Taking all the metal ions into consideration, the observed stability order is $UO_2^{2+} > Be^{2+} > Y^{3+} > La^{3+}$ for log β_2 values in each case. If the metal–ligand bond is considered to be purely electrostatic in nature, the strength of the bond should linearly increase with the increase in ionic potential (Z^2/r) where Z is the effective nuclear charge and r is the radius of the metal ion. Thus the above stability order is

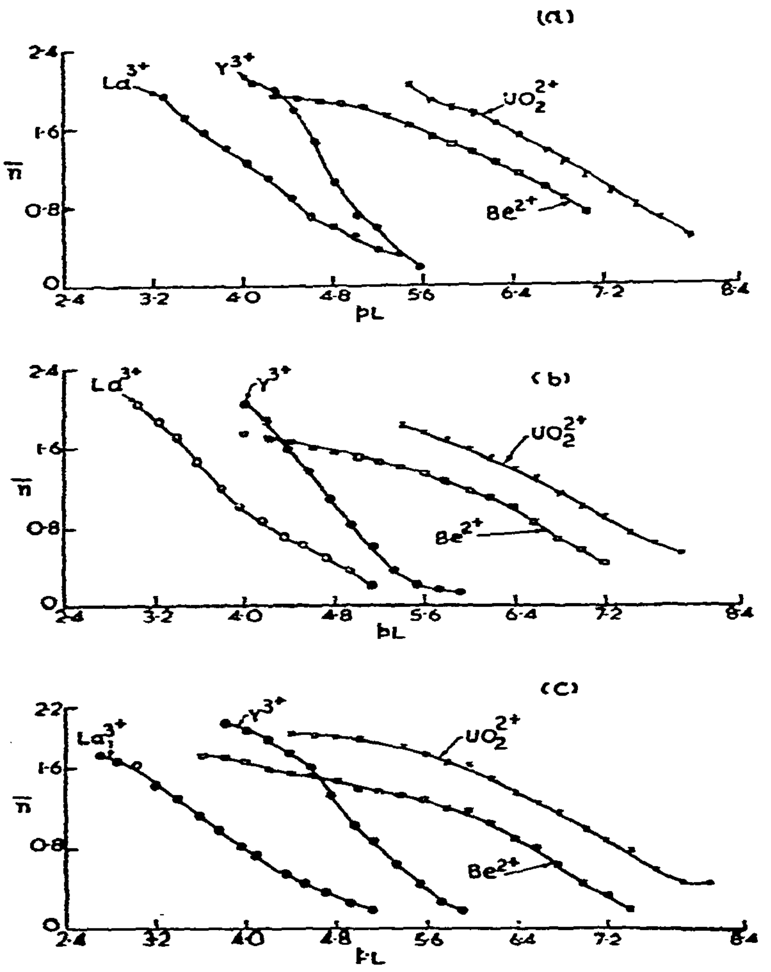

Fig. 1. Formation curves for metal–thioglycolic acid complexes at 35°C. (a) At $\mu = 0.25$ M; (b) at $\mu = 0.15$M; (c) at $\mu = 0.065$M.

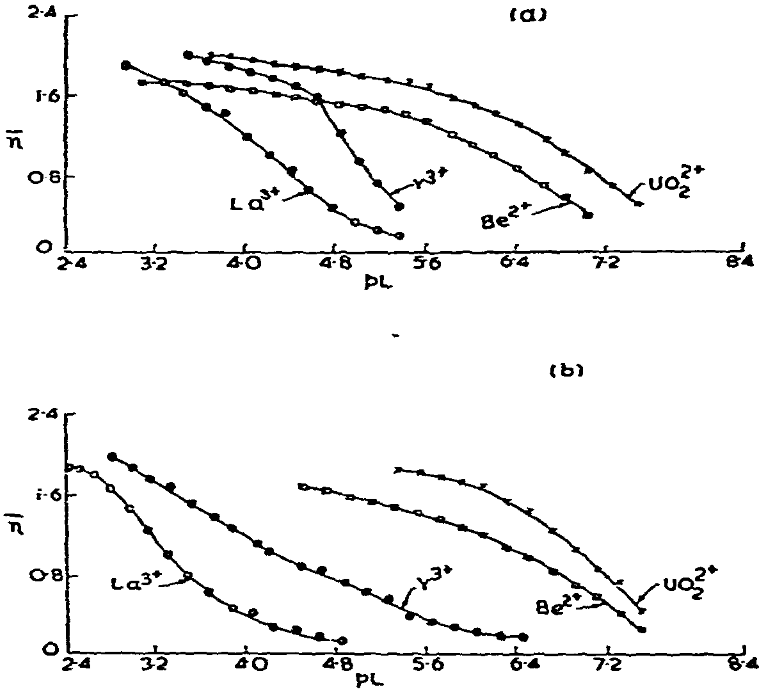

Fig. 2. Formation curves for metal–thioglycolic acid complexes at $\mu = 0.065$ M. (a) At $T = 45$°C; (b) at $T = 25$°C.

justified on the basis of Z^2/r values for these metal ions which are in the sequence $UO_2^{2+} > Be^{2+} > Y^{3+} > La^{3+}$.

From the data (Table 2), it is seen that the values of log β_2 for Y^{3+} complexes are 8.85, 10.02, 10.15 at 25, 35 and 45°C, respectively, and in the case of La^{3+}, the corresponding values are 6.85, 7.64, 8.42 in a solution of an ionic strength of 0.065 M showing that the stabilities gradually increase with rise in temperature for these metal ions and the reactions are more favourable at higher temperatures. However, the log β_2 values are 12.58, 11.84, 11.68 at 25, 35 and 45°C, respectively, for Be^{2+}; 14.03, 13.97 and 13.63 at 25, 35 and 45°C, respectively, in the case of UO_2^{2+} complexes, showing thereby that the stabilities vary inversely with the rise in temperature for Be^{2+} and UO_2^{2+} systems and the reactions are less favourable at higher temperatures.

In the case of La^{3+}, Be^{2+} and UO_2^{2+} complexes, the stability increases with increasing ionic strength. Martin and Paris[11] had already reported that the stabilities of $Cu(gly)_2$ and $Cu(ala)_2$ increased with the increase in ionic strength of the medium. As thioglycolic acid contains –COOH and –SH groups as compared to glycine and alanine which contain –COOH and $-NH_2$ groups, the increased stability in our case is justified on the basis of equal charge on the complex formed, thus decreasing the activity of water.

Thermodynamic functions

The thermodynamic functions for the formation of complexes from equilibrium constants at various temperatures were determined assuming the heat of reaction to be constant over the selected temperature range. Thus the changes in Gibb's free energy were computed using the Van 't Hoff isotherm, while the changes in entropy were evaluated by using the following equations

$$\Delta H = -RS_1$$

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

Where S_1 is the slope of the linear plot of ln K vs. $1/T$. The values are summarized in Table 3. The ΔG, ΔH and ΔS values are not the standard ΔG°, ΔH° and ΔS° which are obtained from the extrapolated values of concentration stability constants to zero ionic strength. The accuracy of ΔH values is ± 0.5 kcal mol^{-1} and that of ΔS values is ± 2 cal deg^{-1} mol^{-1}.

TABLE 3

THERMODYNAMIC FUNCTIONS OF METAL–THIOGLYCOLIC ACID COMPLEXES AT 35°C AND IONIC STRENGTH OF 0.065M

Metal ion	$-\Delta G$ *(kcal mol^{-1})*	ΔH *(kcal mol^{-1})*	ΔS *(cal deg^{-1} mol^{-1})*
Y^{3+}	14.1	22.1	117.5
La^{3+}	10.8	36.6	153.9
Be^{2+}	16.7	−24.4	−25.0
UO_2^{2+}	19.7	−11.1	28.0

The greater the negative value of ΔG, the greater is the stability. The value of ΔG will be higher if ΔH is negative and ΔS is positive. A positive entropy effect, i.e., increase in randomness in system will increase the stability of the complex. Complexation is favoured by entropy change in terms of release of originally bound water molecules[12]. According to Moeller et al.[13] the majority of the rare earth metal ion chelates are entropy stabilized.

In general, the more negative ΔH becomes, the less positive ΔS is. The formation of species which are favoured by enthalpy change, largely retains the primary hydration sphere of the La^{3+} ions and are of outer sphere, ion-pair type. Those complexes, the formation of which is antagonized by enthalpy changes, but favoured by entropy changes, suffer rupture of primary hydration sphere and are of the inner sphere type as described by Grenthe[12].

The values of $-\Delta G$ are 14.1, 10.8, 16.7, 19.7 kcal mol^{-1} in the case of Y^{3+} La^{3+}, Be^{2+} and UO_2^{2+} complexes which are in the order $UO_2 > Be > Y > La$, thus justifying the observed stability order. The values of ΔH and ΔS are positive for Y^{3+}

and La^{3+} complexes. The high positive values of ΔH and ΔS clearly indicate that the reaction is endothermic.

The enthalpy and entropy changes of complex formation of lanthanide ions with charged ligands are often described by using a simple electrostatic model in connection with the Frank and Evans iceberg concept. Species in water solutions are surrounded by a cloud of water molecules with a geometry different from that of bulk water. The complex has a greater radius and reduced charge as compared to the reactants, and therefore, water molecules will be released in the association reactions. It was pointed out by Williams that usually where a high entropy of reaction was observed, the reaction involves a combination of positive and negative ions. In the combination of positive and negative ions, there is a neutralization of charge, so that the complex formed is less hydrated and the remaining water molecules are under less restraint than the free metal cation and ligand anion. Thus the entropy increase favours the formation of complex. Accordingly in the present case, it would, therefore, be evident that increase in entropy is due to the combination of positive and negative ions with displacement of water molecules from hydration sphere of Y^{3+} and La^{3+} ions. Thus Y^{3+} and La^{3+} complexes are stabilized by large entropy changes.

In the case of uranyl complexes, the values of ΔH and ΔS are -11.1 kcal mol^{-1} and 28 cal deg^{-1} mol^{-1}, respectively, showing thereby that both the enthalpy and entropy terms are favourable for the formation of complexes.

The value of ΔH is -24.4 kcal mol^{-1} and that of ΔS is -25 cal deg^{-1} mol^{-1} in the case of Be^{2+} complexes, clearly indicating that the complexes are enthalpy stabilized. The high negative value of ΔH and the negative value of ΔS indicate that Be^{2+} retains the primary hydration and its complexes are of outer sphere, ion-pair type.

REFERENCES

1 A. I. Buser and F. Chang, *Zh. Anal. Khim.*, 16 (1961) 39.
2 V. M. Bhuchar, *Nature*, 191 (1961) 489.
3 G. F. Kirkbright and W. K. Ng, *Anal. Chim. Acta*, 35 (1966) 116.
4 M. V. Reddy and P. K. Bhattacharya, *J. Prakt. Chem.*, 312 (1970) 69.
5 I. Grenthe, *Acta Chem. Scand.*, 16 (1962) 1695.
6 R. Sarin and K. N. Munshi, *J. Inorg. Nucl. Chem.*, 35 (1973) 201.
7 J. Bjerrum, *Metal Ammine Formation in Aqueous Solution*, Hasse & Son, Copenhagen, 1941.
8 M. Calvin and K. W. Wilson, *J. Amer. Chem. Soc.*, 67 (1945) 2003.
9 H. Irving and H. S. Rossotti, *J. Chem. Soc.*, (1954) 2904.
10 H. Irving and H. S. Rossotti, *J. Chem. Soc.*, (1953) 3397.
11 R. P. Martin and R. A. Paris, *C.R. Acad. Sci. Paris*, 258 (1964) 3038.
12 I. Grenthe, *Acta Chem. Scand.*, 18 (1964) 293.
13 T. Moellor, E. R. Birnboum, J. H. Forsberg and R. B. Gayhart, in L. Eyring (Ed.), *Progress in Science and Technology of the Rare Earths*, Vol. 3, Pergamon Press, London, 1968, Ch. 3.