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Stability and Thermodynamics of Zinc Group Metals with Salicyloyl Urea

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The proton ligand stability constant of salicyloyl urea and stability constants and thermodynamic functions of its complexes with Zn(II), Cd(II) and Hg(II) have been determined in methanol-water 20 : 80 (v/v) system. The effect of change of temperature and ionic strength have been studied.

INTRODUCTION

Salicyloyl urea is important from biological point of view due to analgesic property. The phenoxy ion produced from salicyloyl urea can interact with metal ions to give metal complexes. Zn(II) is biologically important due to its role in metalloenzymes while Cd(II) and Hg(II) are toxic[1,2]. The stability constant of complexes of these metal ions with salicyloyl urea have been determined in methanol-water system 20 : 80 (v/v) at different temperatures and different ionic strengths by Bjerrum Calvin[3,4], pH titration technique as adopted by Irving and Rossotti[5,6].

EXPERIMENTAL

Salicyloyl urea was prepared by reacting urea with salicyloyl chloride following the method used for preparation of urea derivatives reported earlier[7].

Salt solutions were prepared by dissolving zinc nitrate, cadmium nitrate and mercuric chloride of BDH 'AnalaR' grade in double distilled water and standardizing to obtain 0.01 M solution. The salicyloyl urea solution (0.05 M) was prepared in methanol. An aqueous solution of sodium perchlorate (1 M) was prepared by direct weighing and was employed to maintain constant ionic strength. Aqueous solution of perchloric acid was standardized against a standard alkali to obtain 0.05 M $HClO_4$. Carbonate-free NaOH solution (0.1 M) was used for the potentiometric titrations. Methanol and double glass distilled water was used to obtain methanol-water medium 20 : 80 (v/v).

Procedure

In order to satisfy the maximum coordination number of the metal ions, the ratio of metal to ligand was kept as 1 : 5. The following three solutions were titrated against standard alkali:

(A) 2.00 ml of 0.05 M $HClO_4$,

(B) A + 2.00 ml of 0.05 M ligand,

(C) B + 2.00 ml of 0.01 M metal.

The total initial volume was 20 ml in each case in which methanol-water ratio was 20 : 80 (v/v). The ionic strength was adjusted by adding 1 M $NaClO_4$. The titration curves were obtained by plotting pH vs volume of alkali added.

RESULTS AND DISCUSSION

The proton ligand stability constant (K_1^H) and stability of metal complexes were calculated by Irving and Rossotti[5] method. The proton ligand stability constant log K_1^H values were obtained by half $\bar{n}$ method and linear extrapolation method. These are found to be in agreement and are given in Table 1.

TABLE 1

PROTON-LIGAND STABILITY CONSTANTS OF SALICYLOYL UREA IN METHANOL : WATER = 20 : 80 (v/v) SYSTEM

Temperature (°C)	Ionic strength M(μ)	Log K_1^H
25	0.00	7.52
	0.05	7.45
	0.10	7.30
	0.50	7.12
35	0.05	7.20
45	0.05	6.95

The maximum value of $\bar{n}$ does not exceed one in all the metal complexes investigated in the present case. This clearly indicates the formation of 1 : 1 complexes of Zn(II), Cd(II) and Hg(II) with salicyloyl urea. The formation of 1 : 1 complexes of Zn(II), Cd(II) and Hg(II) occur in the pH range 5.80–6.80, 6.00–7.40 and 4.10–4.50 respectively.

The stability constants of metal complexes were calculated by half $\bar{n}$ and linear extrapolation methods. The thermodynamic stability constants were obtained at 25°C by plotting log K against $\sqrt{\mu}$ and extrapolating to zero ionic strength. These values are given in Table 2.

The comparison of stability constants at 25°, 35° and 45°C (Table 2) clearly shows that the stability of complexes decreases with rise of temperature and increase of ionic strength. The low temperature favours the formation of these complexes. The perusal of the stability constants

TABLE 2

STABILITY CONSTANTS AND FREE ENERGY CHANGE (ΔG) FOR METAL SALICYLOYL UREA COMPLEXES IN METHANOL-WATER SYSTEM 20 : 80 (v/v)

Metal ion	Temperature (°C)	Ionic strength (M)	Log K_1	$-\Delta G$ Kcal mol^{-1}
Zn^{2+}	25	0.00	4.42	6.03
		0.05	4.10	5.59
		0.10	3.90	5.32
		0.50	3.30	4.50
	35	0.05	3.45	4.60
	45	0.05	2.40	4.22
Cd^{2+}	25	0.00	3.44	4.69
		0.05	3.15	4.29
		0.10	2.95	4.02
		0.50	2.45	3.34
	35	0.05	2.85	4.02
	45	0.05	2.68	3.90
Hg^{2+}	25	0.00	6.02	8.21
		0.05	5.60	7.64
		0.10	5.50	7.50
		0.50	4.78	7.52
	35	0.05	5.15	7.26
	45	0.05	4.72	6.87

(Table 2) shows that the stability constants (log K_1) are in the order

$$Hg(II) > Zn(II) > Cd(II)$$

This order can be explained by making use of the fact that the stability of complexes increases with increase of ionization potential and electronegativity values of metals[8].

The thermodynamic functions such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) associated with complexation were calculated by the following relationships:

$$\Delta G = -2.303\ RT \log K$$

$$\frac{\Delta H}{RT^2} = \frac{d \ln K}{dT}$$

$$\Delta G = \Delta H - T\Delta S$$

The log K values were plotted against 1/T and the slope, S′, of the curve was obtained. The value of ΔH was calculated using the relation $\Delta H = -2.303\, R \times S'$. The values of ΔG, ΔH and ΔS are given in Tables 2 and 3. Both ΔH and ΔS are negative. It clearly suggests that enthalpy term is favourable whereas entropy term is unfavourable for complexation in present investigation.

TABLE 3

THE ENTHALPY CHANGE (ΔH) AND ENTROPY CHANGE (ΔS) ASSOCIATED WITH FORMATION OF METAL SALICYLOYL UREA COMPLEXES IN METHANOL-WATER SYSTEM 20 : 80 (v/v) AT IONIC STRENGTH (μ)=0.05 M

Metal ion	Temperature °C	−ΔH Kcal mol^{-1}	−ΔS Cal deg^{-1} mole^{-1}
Zn^{2+}	25	25.56	67.01
	35		68.05
	45		67.11
Cd^{2+}	25	9.53	17.58
	35		17.88
	45		17.70
Hg^{2+}	25	18.82	37.52
	35		37.53
	45		37.58

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