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A THERMODYNAMIC STUDY OF THE COMPLEXATION REACTION OF BERYLLIUM(II), MAGNESIUM(II) AND CALCIUM(II) WITH 3-HYDROXY-2-NAPHTHOIC ACID

R. S. SANDHU AND KANWALJIT SINGH
Department of Chemistry, Guru Nanak Dev University, Amritsar 143005 (India)
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ABSTRACT

The thermodynamic stability constants and thermodynamic parameters for the complexation reaction of Be^{2+}, Mg^{2+} and Ca^{2+} with 3-hydroxy-2-naphthoic acid have been determined pH metrically in a 70% v/v dioxane–water medium in the presence of potassium nitrate. The study showed the formation 1:1 and 1:2 complexes of Be^{2+}, Mg^{2+} and 1:1 complex of Ca^{2+} with 3-hydroxy-2-naphthoic acid. The order of overall stability is $Be^{2+} > Mg^{2+} > Ca^{2+}$

INTRODUCTION

The complexes of 3-hydroxy-2-naphthoic acid with different metal ions have been studied by various workers under different experimental conditions[1–4]. Recently, complexes of lanthanides with 3-hydroxy-2-naphthoic acid have been prepared in which coordination through oxygen of hydroxy group of the acid has been indicated[5,6]. Mehrotra et al.[6] and Makitie[7] have reported the stability constants of Be^{2+} complex of 3-hydroxy-2-naphthoic acid in a 50% v/v ethanol–water medium. In the present study, the stability constants of Be^{2+}, Mg^{2+} and Ca^{2+} with 3-hydroxy-2-naphthoic acid have been determined in a 70% V/V dioxane–water medium at three temperatures and at an ionic strength of 0.05, 0.10 and 0.15M KNO_3. The thermodynamic formation constants and thermodynamic parameters have been evaluated therefrom.

EXPERIMENTAL

The pH titration technique of Calvin-Wilson[8] as modified by Irving and Rossotti[9] has been employed in the present investigation. All chemicals used were of BDH AnalaR quality. Dioxane was purified by the method described by Vogel[10]. The double-distilled CO_2 free water was used in all experimental work. A photovolt Digicord pH meter having a sensitivity of 0.002 was calibrated by suitable buffers before use. The thermostat bath temperature was maintained at 20±0.1, 30±0.1 and 40±0.1 °C and titrations were carried out in a 70% V/V dioxane–water mixture.

The three solutions were prepared as follows: A, 1.0×10^{-2}M HNO_3; B, 1.0×10^{-2}M $HNO_3 + 5.0 \times 10^{-2}$M ligand; C, 1.0×10^{-2}M $HNO_3 + 5.0 \times 10^{-2}$M ligand $+1.0\times10^{-2}$M metal nitrate solution. An appropriate quantity of potassium nitrate (2.0M) was added to maintain the desired ionic strength of 0.05, 0.10 and 0.15M. The initial volume of the solution was 50 ml in all cases. The above solutions were titrated against 0.15M KOH prepared in a 70% V/V dioxane–water mixture. In calculations, the concentrations were corrected for changes in volume produced by the addition of alkali during titration. The shapes of the curves were as usual.

RESULTS AND DISCUSSION

$\bar{n}_H$, $\bar{n}$, pL were calculated by employing the relationship derived by Irving and Rossotti[9]. The practical proton–ligand stability constant, $\log {}^{P}K_2^H$ was obtained from the proton–ligand formation curve plotted between $\bar{n}_H$ versus pH as Bjerrum half-integral method and pointwise calculation method. In the case of 3-hydroxy-2-naphthoic acid, since there are few values of $\bar{n}_H$ below one, the value of $\log {}^{P}K_1^H$ was obtained from the relationship

$$\log {}^{P}K_1^H\,{}^{P}K_2^H = 2\text{pH (at } \bar{n}_H = 1).$$

The plots of $\bar{n}$ versus pL for the complexes indicate that the values of $\bar{n}$ obtained are of the order 2 in case of Be^{2+} and Mg^{2+}. This suggests that Be^{2+} and Mg^{2+} forms two types of complexes in the proportions 1:1 and 1:2 with the ligand. However, in the case of the Ca^{2+} complex the $\bar{n}$ value remains less than 1 indicating the formation of a 1:1 complex only. Metal ligand stability constants $\log K_1$ and $\log K_2$ were calculated from the formation curves obtained by plotting graphs between $\bar{n}$ and pL using Bjerrum half integral method, interpolation at various $\bar{n}$ values and graphical methods[11] as extended to the water–dioxane mixture by Van Uitert and Haas[12]. The values of $\log {}^{P}K_1^H$, $\log {}^{P}K_2^H$, $\log K_1$ and $\log K_2$ obtained by different methods agree fairly well and their average values are summarized in Table 1. The data show an increase in $\log K_1$ and $\log K_2$ values with the increase in temperature which indicate that higher temperatures are favourable for complex formation. The order of overall stability is $Be^{2+} > Mg^{2+} > Ca^{2+}$ as expected from their electronic configuration. Since the charge to radius ratio decreases, the stability also decreases. This may be the reason for the formation of the 1:1 complex only in the case of Ca^{2+}. The stability decreases with an increase in ionic strength. The thermodynamic values of stability constants were evaluated by extrapolation to zero ionic concentration from plots of $\log K$ versus $\sqrt{\mu}$ (Table 2). The calculated error in stability constant is $\pm 0.05 \log K$.

The values of overall changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) accompanying complexation have been determined using the Gibbs-Helmoltz equation (Table 1). The values of ΔG° were obtained from the equation $\Delta G^\circ = -RT \ln \beta$. ΔH° was determined with the help of an isobar equation:

$$\frac{d \ln \beta}{d(1/T)} = \frac{\Delta H^\circ}{RT^2}$$

TABLE 1

PROTONATION CONSTANTS OF THE LIGAND, STEPWISE AND OVERALL METAL-LIGAND STABILITY CONSTANTS OF THE COMPLEXES AND THERMODYNAMIC PARAMETERS AT THREE TEMPERATURES AND AT 0.1M IONIC STRENGTH

Metal ion	*Protonation/metal ligand stability constants*	*Temperature*			$\Delta G°$ (*kcal mol*$^{-1}$)			$\Delta H°$ (*kcal mol*$^{-1}$) *at 30°C*	$\Delta S°$ (*cal mol*$^{-1}$ *deg*$^{-1}$) *at 30°C*
		20°C	*30°C*	*40°C*	*20°C*	*30°C*	*40°C*		
H^+	$\log {}^{P}K_1^H$	8.90	9.86	10.81					
	$\log {}^{P}K_2^H$	2.10	2.14	2.19					
	$\log {}^{P}\beta_2^H$	11.00	12.00	13.00					
Be^{2+}	$\log K_1$	11.77	13.05	14.30	15.78	18.09	20.48		
	$\log K_2$	6.46	8.52	9.11	8.66	11.82	13.06		
	$\log \beta_2$	18.23	21.57	23.41	24.44	29.91	33.54	121.16	498.58
Mg^{2+}	$\log K_1$	4.12	4.85	5.78	5.52	6.72	8.27		
	$\log K_2$	3.11	4.08	5.43	4.17	5.66	7.78		
	$\log \beta_2$	7.23	8.93	11.21	9.69	12.38	16.05	83.96	317.95
Ca^{2+}	$\log K_1$	3.61	4.42	5.16	4.84	6.13	7.39	32.95	128.97

TABLE 2

STABILITY CONSTANTS OF 3-HYDROXY-2-NAPHTHOIC ACID AT 30°C

Ionic strength	*log K_n*	H^+	Be^{2+}	Mg^{2+}	Ca^{2+}
0.15M	log K_1	9.68	12.58	4.22	3.25
	log K_2	2.12	7.56	3.87	—
	log β_2	11.80	20.14	8.09	—
0.10M	log K_1	9.86	13.05	4.85	4.42
	log K_2	2.14	8.52	4.08	—
	log β_2	12.00	21.57	8.93	—
0.05M	log K_1	10.23	13.65	5.33	5.91
	log K_2	2.17	10.28	4.63	—
	log β_2	12.40	23.93	9.96	—
→0	log K_1	10.98	15.09	6.88	9.40
	log K_2	2.21	13.83	5.65	—
	log β_2	13.24	29.00	12.50	—

which may be rewritten as

$$\frac{d(\log \beta)}{d(1/T)} = \frac{-\Delta H^\circ}{4.576}$$

The values of log β obtained at different temperatures were plotted as a function of $1/T$. The gradient of the tangent drawn at 30°C was determined and equated to $-\Delta H^\circ/4.576$. ΔH° was thus obtained. ΔS° was then evaluated from the relation:

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

The values of ΔG° and ΔH° are accurate to 1.5 kcal mol^{-1} and ΔS° to ± 5 cal mol^{-1} deg^{-1}. The free energies of formation (ΔG°) of the complexes have more negative values with an increase in temperature showing that complex formation is a spontaneous process. The positive ΔH° values for the complexes indicate an endothermic reaction and explain why the formation constants have higher values at higher temperatures. The large entropy change (ΔS°) accompanying the complexation reaction is due to liberation of water molecules from the hydration sphere of the metal during complex formation.

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