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Note

Stability constants and thermodynamic functions of zinc(II), cadmium(II) and mercury(II) chelates of 1-hydroxy-2-naphthoic acid

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The metal chelates of 1-hydroxy-2-naphthoic acid have been studied earlier by various workers[1–4]. The stability constants and some thermodynamic functions of the chelates of Zn^{2+}, Cd^{2+} and Hg^{2+} formed with 1-hydroxy-2-naphthoic acid are reported in this communication.

EXPERIMENTAL

Materials

All chemicals used were of B.D.H. AnalaR quality. The twice-distilled conductivity water was used in all experimental work. The solution of 1-hydroxy-2-naphthoic acid (0.05M) was prepared in absolute alcohol, whereas the solutions of nitric acid, potassium nitrate and metal nitrates were prepared in conductivity water by dissolving the requisite quantities. Potassium nitrate (1.0M) solution was used to maintain constant ionic strength at 0.1M.

Procedure

The titrations were carried out at 30, 35 and 40°C. The pH was measured on a digicord pH meter M 120. For each set of experiments three titrations were performed by the Calvin-Bjerrum[5,6] pH titration technique as modified by Irving and Rossotti[7].

(i) *Acid titration.* Nitric acid (0.01M, 5.00 ml)+potassium nitrate (1.0M, 4.95 ml)+absolute alcohol (35.00 ml)+conductivity water (5.05 ml).

(ii) *Reagent titration.* Nitric acid (0.01M, 5.00 ml)+potassium nitrate (1.0M, 4.35 ml)+reagent (0.05M, 5.00 ml)+absolute alcohol (30.00 ml)+conductivity water (5.65 ml).

(iii) *Metal titration.* Nitric acid (0.01M, 5.00 ml)+potassium nitrate (1.0M, 4.20 ml)+reagent (0.05M, 5.00 ml)+metal solution (0.01M, 5.00 ml)+absolute alcohol (30.00 ml)+conductivity water (0.80 ml).

The initial volume of the solution was 50 ml in each case. All the above solutions were titrated against 0.1M potassium hydroxide solution at the above-mentioned temperatures in a thermostat. After addition of each portion of alkali, the pH was noted and a correction suggested by Van Uitert and Haas[8] was applied to it. The plots of the pH of the solution against the volume of the alkali added gave curves of the usual shape.

RESULTS AND DISCUSSION

The proton ligand formation curve was obtained by plotting the degree of formation ($\bar{n}_H$) of the proton–ligand complex against pH value, using the relationship derived by Irving and Rossotti[7].

The practical proton–ligand stability constant ($\log {}^{P}K_2^H$) of the ligand has been obtained as Bjerrum half-integral method and also by pointwise calculation method at different points using the following equation:

$$\log {}^{P}K_2^H = \mathrm{pH} + \log (\bar{n}_H - 1)/(2 - \bar{n}_H)$$

In the case of 1-hydroxy-2-naphthoic acid, since there are very few values of $\bar{n}_H$ below one, the value of $\log {}^{P}K_1^H$ has therefore, been calculated by using the following relationship:

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

The complex–ligand formation curve was then obtained by plotting the degree of formation of the complex ($\bar{n}$) versus–log [ligand] using the relationship derived by Irving and Rossotti[7].

The metal–ligand stability constants were determined by the Bjerrum half-integral method[6] and also by pointwise calculation method using the following equations:

$$\log K_1 = \mathrm{pL} - \log (1 - \bar{n})/\bar{n}$$

and $\log K_2 = \mathrm{pL} - \log (2 - \bar{n})/(\bar{n} - 1)$

The values of overall changes in free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) accompanying complexation have been determined using the temperature cœfficient and Gibbs-Helmholtz equation[9].

The value of $\Delta G°$ was obtained from the expression $\Delta G° = -RT \ln \beta$. $\Delta H°$ was determined with the help of an isobar equation.

$$\frac{\mathrm{d} \ln \beta}{\mathrm{d}T} = \frac{\Delta H°}{RT^2}$$

which may be rewritten as

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

The values of $\log \beta$ obtained at different temperatures were plotted as a function of $1/T$. The gradient of the tangent drawn at the point corresponding to 35°C was

TABLE 1

PROTONATION CONSTANTS OF THE LIGAND; STEPWISE AND OVERALL METAL–LIGAND STABILITY CONSTANTS OF THE COMPLEXES AND THERMODYNAMIC PARAMETERS AT THREE TEMPERATURES

Metal ion	*Protonation constants/ metal–ligand stability constants*	*Temperature*			$-\Delta G^\circ$ ($kJ\ mol^{-1}$)			ΔH° ($kJ\ mol^{-1}$) *at 35°C*	ΔS° ($J\ mol^{-1}\ {}^\circ C^{-1}$) *at 35°C*
		30°C	*35°C*	*40°C*	*30°C*	*35°C*	*40°C*		
	$\log {}^{P}K_1^H$	10.40	10.97	11.35					
	$\log {}^{P}K_2^H$	2.60	2.63	2.65					
	$\log {}^{P}\beta^H$	13.00	13.60	14.00					
Zn^{2+}	$\log K_1$	7.49	8.15	8.81	43.41	48.01	52.74		
	$\log K_2$	6.85	7.64	8.20	39.70	45.01	49.09	460.78	1798.05
	$\log \beta$	14.34	15.79	17.01	83.11	93.02	101.83		
Cd^{2+}	$\log K_1$	6.68	7.28	7.78	38.72	42.89	46.58		
	$\log K_2$	5.75	6.12	6.84	33.32	36.05	40.95	382.54	1498.31
	$\log \beta$	12.43	13.40	14.62	72.04	78.94	87.53		
Hg^{2+}	$\log K_2$	6.89	8.63	9.16	39.93	50.94	54.84	391.23	1435.29

determined and equated to $-\Delta H°/4.576$. The value of $\Delta H°$ was thus obtained. $\Delta S°$ was then evaluated from the relation.

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

The mean values of protonation constants, stability constants and thermodynamic parameters are summarized in Table 1.

The formation curves ($\bar{n}$ vs. pL) show that $\bar{n}$ approaches a value of 2 for Zn^{2+}, Cd^{2+} and Hg^{2+} chelates of 1-hydroxy-2-naphthoic acid indicating the formation of both 1:1 and 1:2 complexes. The data show an increase in the values of $\log {}^{P}K_1^H$, $\log {}^{P}K_2^H$, $\log K_1$ and $\log K_2$ with increase in temperature. The order of overall stability of these complexes is $Zn^{2+} > Cd^{2+} > Hg^{2+}$ at 30, 35 and 40°C. This is to be expected since the metal with a large ionic potential, i.e., charge-to-radius ratio should form more stable complexes. As on moving down the group, the charge-to-radius ratio decreases, the stability also decreases. The free energies of formation ($\Delta G°$) of the complexes have more negative values with the increase of temperature, showing that complex formation is a spontaneous process. The formation of all the complexes is an endothermic reaction and it explains the increase in the values of formation constants with rise in temperature. The entropy change ($\Delta S°$), accompanying the formation of a complex is positive in all cases.

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