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Note

PHYSICO-CHEMICAL STUDIES ON THE COMPOSITION AND STABILITY CONSTANTS OF Zn(II), Cd(II) AND Hg(II) L-LYSINE MONOHYDROCHLORIDE COMPLEXES

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L-Lysine monohydrochloride complexes of divalent metals like Zn(II), Cd(II) and Hg(II) have been investigated potentiometrically in aqueous. 0.1 M NaOH solution using the Bjerrum–Calvin technique at 20, 30 and 40°C. The refinement of stability constants was made by the least-squares method. The trend in the stability of these 1 : 2 metal complexes was found to be: Zn(II) > Hg(II) > Cd(II). Zn(II), Cd(II) and Hg(II) form 1 : 2 complexes at pH 8 to 9.

Sharma and co-workers [1–4] have studied metal complexes of amino acids which have been found useful in biological and pharmaceutical fields. The present communication describes the chemistry of Zn(II), Cd(II) and Hg(II) complexes with L-Lysine monohydrochloride, their composition, stability constants and free energy at different temperatures.

EXPERIMENTAL

L-Lysine monohydrochloride, referred to herein as HA, was obtained from B.D.H. (Fluka). All other chemicals were prepared in doubly distilled carbon-dioxide-free water. The experimental procedures were the same as those reported earlier [1–4]; pH measurements were made on a 'c' pH-meter with a glass–calomel electrode assembly in a nitrogen atmosphere. The temperature of the cell was maintained by a thermostat (U_3 type, German) having an accuracy of ± 0.1°C.

RESULTS

Stoichiometry

The composition of the complex formed during the interaction of metal ions with L-lysine monohydrochloride was established by measuring the

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magnitude of proton displacement during titration of the ligand in the absence and presence of metal ions at different ratios indicating complex formation.

$$M^{n+} + HA \rightarrow MA^{(n-1)} + H^+$$

Where M^{n+} stands for Zn(II), Cd(II) and Hg(II), when the metal ion and ligand are mixed in the ratios 1 : 4, 1 : 2 and 1 : 1 inflections are obtained at $\bar{n} = 0.5$, 1.0 and 2.0, respectively ($\bar{n}$ being the mole of NaOH per mole of HA). Inflections suggest the formation of MA_2 corresponding to 1 : 2 complexes with considerable overlapping according to the equations

$$\begin{array}{lcl} M^{2+} + HA + OH^- & \rightarrow & Ma^+ + HOH \\ MA^+ + HA + OH^- & \rightarrow & MA_2 + HOH \\ \hline M^{2+} + 2\,HA + 2\,OH^- & \rightarrow & MA_2 + 2\,HOH \end{array}$$

The 1 : 2 complexes were formed spontaneously.

Stability constants

Stability constants of L-lysine monohydrochloride complexes with divalent Zn(II), Cd(II) and Hg(II) were determined using the Bjerrum–Calvin technique [5,6] and further refined by least-squares treatment.

At any pH, the free ligand concentration [A], was calculated from the relation.

$$[A] = \frac{[\text{ligand}]_{\text{total}} - [\text{ligand}]_{\text{bound}}}{(H^+/K_a) + 1}$$

where K_a is the dissociation constant [7] of HA. The values of log k_1 and k_2 were obtained from the formation curves at $\bar{n} = 0.5$ and 1.5, respectively.

The constants are best evaluated by the least-squares method.

$$\frac{n}{(\bar{n} - 1)(L)} = \frac{(2 - \bar{n})}{(\bar{n} - 1)} k_1 k_2 - k_1$$

The values of the stability constants at various temperatures and obtained by different methods are summarised in Table 1.

Thermodynamic functions

The values of the overall changes in free energy, ΔG, enthalpy ΔH, and entropy, ΔS, accompanying complex formation have been determined using the standard equations

$$\Delta G = -RT \log B$$

$$\Delta H = \frac{2.305\, RT\, T_2 \log k_2 / \log k_1}{(T_2 - T_1)}$$

TABLE 1

Metal–ligand stability constants and thermodynamic functions for Zn(II), Cd(II) and Hg(II) complexes of L-lysine

System	Temperature (°C)	Bjerrum method		Least-squares method		ΔG (kJ mole^{-1})	ΔH (kJ mole^{-1})	ΔS (e.u.)
		$\log k_1$	$\log k_2$	$\log k_1$	$\log k_2$			
Zn–Ha	20	8.80	4.60	8.92	4.50	−74.6		
	30	8.40	4.20	8.40	4.2	−72.0	−241.2	−132.3
	40	7.4	3.80	7.40	3.80	−67.0		
Cd–HA	20	7.3		7.80		−43.4		
	30	6.8		7.60		−43.4	−122.4	−62.0
	40	6.2		6.90		−40.7		
Hg–HA	20	8.0	5.90	8.00	5.95	−77.8		
	30	7.00	5.90	7.94	5.80	−79.0	−205.0	−99.0
	40	7.36	4.80	7.35	5.28	−74.8		

Uncertainty limit for $k_1 = 0.4$ and $k_2 = 0.3$ for thermodynamic functions $\Delta G = 0.3$ kJ mole^{-1} and $\Delta H = 0.5$ kJ mole^{-1}.

and

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

The values of the thermodynamic parameters are given in Table 1.

DISCUSSION

A comparison of the stability constants indicates that the values are slightly higher at 20°C as compared to 30 and 40°C, indicating that low temperature is favourable for complex formation. The trend in the stability of the metal complexes is Zn(II) > Hg(II) > Cd(II), in the case of the 1 : 2 complexes this is in agreement with the accepted view that the stability of metal complexes depends on the metallic nuclear charge (atomic number), the screening constant and the ionic radius.

Complex formation is a spontaneous process which is evident from the negative values of ΔG: the negative values of ΔH also ensure that the reaction is an exothermic process.

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