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Note

DETERMINATION OF STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF L-LYSINE MONOHYDROCHLORIDE WITH Sm(III), Bi(III) AND Gd(III) METAL IONS

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Recently, interest has developed in metal complexes [1–6] of L-lysine monohydrochloride. A survey of the literature reveals that L-lysine has found application in both qualitative and quantitative estimations of various metals [7–9].

In this note we report the stepwise coordination and thermodynamic parameters of Sm(III), Bi(III) and Gd(III) with L-lysine monohydrochloride.

EXPERIMENTAL

L-lysine monohydrochloride was obtained from Fluka (Switzerland) and all metal salts were obtained from BDH. Solutions were prepared in water distilled over alkaline potassium permanganate.

The pH-metric investigations were carried out in aqueous media in the temperature range 15–30 °C (±0.1 °C) using carbonate-free 1 M NaOH. A constant ionic strength of 1 M was maintained by adding an appropriate quantity of potassium nitrate–chloride solution. The stability constants of the metal and proton complexes were determined using the Bjerrum–Calvin technique [10]. The pH of the solution was measured with a Metram Harison E-520 pH-meter.

RESULTS AND DISCUSSION

The ligand dissociates as

$$NH_2CH(CH_2)_4NH_2COOH \cdot HCl \rightleftharpoons NH_2CH(CH_2)_4NH_2COOH + HCl$$

$$NH_2CH(CH_2)_4NH_2COOH \rightleftharpoons NH_2CH(CH_2)_4NH_2COO^- + H^+$$

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The carboxylic group of the acid does not form the conjugate base intermolecularly, indicating the virtual absence of any dipolar form.

The presence of a single inflexion on titration of the acid with strong base in aqueous media confirms the foregoing view.

Examination of the pH-metric curves reveals a separation of metal ligand curves from acid curves. This confirms that the proton liberation is due to complexation; the value of n^- increases gradually in all cases. This demonstrates the involvement of the anionic form of the acid in complexation; the $n^- = 3$ value for the Sm(III), Bi(III) and Gd(III) L-lysine mono + hydrochlorides indicates the presence of complexes of 1 : 3 stoichiometry. An analysis of the formation curves (n^- vs. pL) indicates that the successive stability constants are not very different. Therefore calculations of stepwise formation cannot be carried out using the Bjerrum integral method ($\log K_1/K_2 = 2.5$).

Furthermore, the shapes of the formation curves confirm the similarity in the successive formation constants. Even the systems of higher complexity (Sm(III), Bi(III) and Gd(III) L-lysine monohydrochloride ($n^- = 3$)) do not fulfil the conditions for K_1 and K_2 (i) $\log K = -\log(L^-)$ at $n^- = 0.5$, (ii) $-\Delta G = RT \log K$.

THERMODYNAMIC FUNCTIONS

The value of $-\Delta G^{\ominus}$ for Sm(III) decreases with an increase in temperature. However, the values of $\Delta G^{\ominus}$ for Bi(III) and Gd(III) L-lysine monohydrochlorides increase with an increase in temperature. The enthalpy $\Delta H^{\ominus}$ is positive for the Sm(III) system indicating the endothermic nature of these reactions. The positive value of $\Delta S^{\ominus}$ for Bi(III) and Gd(III) only favours the formation of the complexes [11]. Table 1 contains the mean values of the

TABLE 1

Thermodynamic functions and stability constants of metal L-lysine monohydrochloride systems

Metal ion	Stability constants		$-\Delta G$ (kcal mol^{-1})		$\Delta H^{\ominus}$ at 30 °C (kcal mol^{-1})	$\Delta S^{\ominus}$ at 30 °C (cal k^{-1} mol^{-1})
	15 °C	30 °C	15 °C	30 °C		
Sm(III)	K_1 5.26	4.84	7.25	6.66	−21.84	−57.22
	K_2 2.57	2.55				
Bi(III)	K_1 5.15	5.26	6.98	7.17	+2.39	+31.80
	K_2 2.97	2.93				
Gd(III)	K_1 3.02	2.35	10.88	11.72	+2.03	+46.77
	K_2 2.76	3.22				

stability constants of the metal and proton complexes at different temperatures, and the thermodynamic functions.

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REFERENCES

1 A.K. Jain, K.D. Jain and U. Sharma, J. Indian Chem. Soc., 57 (1980) 963.
2 U. Sharma and N. Chandra, Thermochim. Acta, 59 (1982) 125.
3 N. Chandra and U. Sharma, Thermochim. Acta, 62 (1983) 125.
4 K.D. Jain and U. Sharma, J. Indian Chem. Soc., 63 (1986) 777.
5 U. Sharma, Acta Ciencia Indica, Sect. C, 113(1) (1987) 45.
6 U. Sharma and K.D. Jain, Indian J. Phys. Nat. Sci., Sect. A, 5 (1985) 61.
7 K. Ward, Diss. Abstr. Int. B, 30(4) (1969) 1569.
8 E. Doody, J. Am. Chem. Soc., 74 (1952) 4184.
9 A. Aziz Khan and W.U. Malik, Curr. Sci. (India), 29 (1960) 135.
10 J. Bjerrum, Metal Amine Formation in Aqueous Solutions, Husse, Copenhagen, 1941.
11 S.S. Sawhney and N. Chandra, Thermochim. Acta, 66 (1983) 369.