

## Note

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### 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.

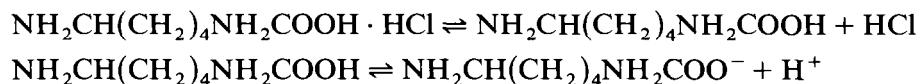
#### EXPERIMENTAL

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 ( $\pm 0.1^\circ\text{C}$ ) 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



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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		$-\Delta G$		$\Delta H^\ominus$ at 30°C (kcal mol <sup>-1</sup> )	$\Delta S^\ominus$ at 30°C (cal k <sup>-1</sup> mol <sup>-1</sup> )
	15°C	30°C	(kcal mol <sup>-1</sup> )			
			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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