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Note

STEPWISE STABILITY CONSTANTS OF URANYL(II) AND THORIUM(IV) COMPLEXES OF L-LYSINE MONOHYDROCHLORIDE

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In continuation of earlier investigations on the metal complexes [1–7] of L-lysine monohydrochloride, this communication studies the stoichiometry, stepwise stability constants and thermodynamic parameters of UO_2^{2+} and Th^{4+} complexes with L-lysine monohydrochloride for which no reference could be traced in the literature.

EXPERIMENTAL

The usual method of synthesising these chelates has been described earlier [1]. The experimental procedure involved a series of pH-metric titrations of 4 mM HA containing 4 mM $HClO_4$ in the absence and presence of 1, 2 and 4 mM metal ion against standard (0.1 M) NaOH.

pH-measurements were made on a Toshniwal digital pH-meter with a glass calomel electrode assembly (accuracy ±0.1 pH units). The temperature of the cell was maintained by a thermostat (U_3-type, Germany) having an accuracy of ±0.1°. Requisite quantities of $NaClO_4$ were added to the solution mixtures to maintain a constant ionic strength (0.1 M). The final volumes of all mixtures were brought to 25 ml with doubly distilled water.

RESULTS AND DISCUSSION

Stoichiometry

To establish the stoichiometry of the complex species formed during interaction of metal ion and HA, the magnitude of proton displacement was determined by titrating the solution containing different ratios of metal ion and HA against 0.1 M NaOH.

The inflection at $m = 1$ in the free ligand titration curve corresponds to the titrability of the proton of the –COOH group under experimental conditions, which was present in a zwitterionic form. The addition of an

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TABLE 1

Stepwise metal ligand stability constants and thermodynamic parameters of UO_2(II) and Th(IV) complexes of L-lysine monohydrochloride

	UO_2(II) complexes			Th(IV) complexes		
	20°C	30°C	40°C	20°C	30°C	40°C
log K_1	7.90	7.80	7.71	–	–	–
log K_2	7.00	6.90	6.00	8.50	8.52	8.60
log K_3				8.20	8.25	8.29
log K_4				5.00	5.69	5.99
ΔG (kcal mol^{-1})	−20.00			−30.90		
ΔH (kcal mol^{-1})	−10.58			24.50		
ΔS (cal K^{-1} mol^{-1})	−31.91			182.67		

equimolar concentration of metal ion greatly alters the shape of the free ligand titration curve indicating complex formation resulting in a lowering of the buffer region due to proton displacement.

$$UO_2^{2+} + HA \rightleftharpoons UO_2A^+ + H^+ \qquad \text{(i)}$$

$$Th^{4+} + HA \rightleftharpoons Th(A)^{3+} + H^+ \qquad \text{(ii)}$$

i.e., 1 : 1 and 1 : 2 complexes are formed simultaneously and in all the above cases metal complexes may disproportionate at higher pH values (9.0) to give normal metal hydroxides.

STABILITY CONSTANTS

Calvin and Malchior's [8] extension of Bjerrum's method [9] has been employed for the determination of stability constants of the complexes at 20, 30 and 40°C and ionic strength, $\mu = 0.1$ M $NaClO_4$ and their values are given in Table 1. The formation curves obtained at different temperatures by plotting $\bar{n}$ vs. log $[A]$ reveal the formation of 1 : 1 and 1 : 2 complexes for the UO_2^{2+}–HA system and 1 : 2, 1 : 3 and 1 : 4 for the Th^{4+}–HA system.

THERMODYNAMIC FUNCTIONS

The free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying complexation reactions have been determined at 30°C with help of the Gibbs–Helmholtz and isobar equations [10], $G = RT$ log β (and recorded in Table 1). ΔH is determined with the help of an isobar $d(\log \beta)/d(1/T) = -\Delta H/4.57 \cdot \Delta S$ is then evaluated from the relation $\Delta S = \Delta H - \Delta G/T$

It is observed from Table 1 that the value of stability constants of UO_2^{2+} complexes decrease with increasing temperature showing that the complexation reaction is exothermic, whereas in the case of Th^{4+} complexes, the log K stability constant values increase with temperature indicating an endothermic process. These observations are confirmed by negative value of ΔH for the UO_2^{2+} complex and positive values for Th^{4+}. The negative values of ΔG in both cases indicate that the reaction proceeds spontaneously. The positive ΔS values (Table 1) obtained indicate that the entropy factor strongly favours chelate formation, and stabilises the complex due to the liberation of water molecules from the ion accompanying complexation.

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