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Note

Complexation reaction of metal ions with peptide systems. I. Potentiometric study of the complexes of copper(II), nickel(II) and cobalt(II) with *N*-benzoyl-L-leucine

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The metal complexes of amino acids and peptides have provided both coordination chemists and biochemists with grist for their experimental mills for a long time[1]. The stability constants of complexes of amino acids with metal ions have been reported in the literature[2, 3]. But no work appears to have been reported for complexes of *N*-benzoyl-L-leucine. The present paper deals with the study of complexes of Cu^{2+}, Ni^{2+} and Co^{2+} with *N*-benzoyl-L-leucine in 50% v/v dioxane–water medium at three temperatures and at an ionic strength of 0.1 M KNO_3. The formation constants and thermodynamic parameters have been evaluated therefrom.

EXPERIMENTAL

The pH titration technique of Calvin and Wilson[4] as modified by Irving and Rossotti[5] has been employed in this work. All chemicals used were either B.D.H. or Aldrick Analar quality. *N*-Benzoyl-L-leucine was prepared by the method described in literature[6] and the dioxane was purified before use[7]. Double-distilled CO_2-free water was used in the preparation of solutions. The solution of *N*-benzoyl-L-leucine was prepared in pure dioxane. Metal nitrate solutions were standardised by the EDTA method before use. All pH metric titrations were carried out in 50% v/v dioxane–water at 20 ± 0.1, 30 ± 0.1, and 40 ± 0.1 °C in a thermostated bath. A Toshniwal pH meter CL 46, having a sensitivity of 0.01 units, was calibrated with suitable buffers before use.

The mole ratio of metal to ligand was kept at 1 : 5 in order to fulfil the maximum coordination number of the metal. The following solutions (total volume 50 ml) were prepared.

A 2.5 ml of 1.0×10^{-2} M HNO_3
B 2.5 ml of 1.0×10^{-2} M HNO_3 + 5 ml of 2.5×10^{-2} M ligand
C 2.5 ml of 1.0×10^{-2} M HNO_3 + 5 ml of 2.5×10^{-2} M ligand + 2.5 ml of 1.0×10^{-2} M metal nitrate

An ionic strength of 0.1 M was maintained by the addition of the calculated amount of KNO_3 (1.0 M). The above solutions were titrated against 0.05 M KOH prepared in 50% v/v dioxane–water. The plots of pH vs. the volume of the alkali required to obtain the corresponding pH change were plotted. The shapes of the titration curves were as usual.

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[5]. The proton–ligand stability constant (carboxylic functional group) has been obtained by a Bjerrum half integral, pointwise calculation method and by graphical methods[8, 9]. Similarly, formation constants have been obtained by plotting $\bar{n}$ vs. pL. The values of $\bar{n}$, the average number of ligands attached per metal ion are calculated from the equation of Irving and Rossotti[5], i.e.

$$\bar{n} = \frac{(V''' - V'')(N + E^0)}{(V^0 + V')\,\bar{n}_H\,T^0_M} \tag{1}$$

and the free ligand exponent pL has been calculated from the equation

$$pL = \log_{10}\left\{\frac{\sum_{n=0}^{n=J} \beta^H_n \left(\frac{1}{\text{antilog } B}\right)^n}{T^0_L - \bar{n}\,T^0_M} \cdot \frac{V^0 + V'''}{V^0}\right\} \tag{2}$$

The value of $\bar{n}$ approaches 1 for the complexes of *N*-benzoyl-L-leucine with Cu^{2+}, Ni^{2+} and Co^{2+} which suggests the formation of 1 : 1 complexes. The value of the concentration stability constants at different temperatures and at 0.1 M ionic strength are summarized in Table 1. The order of stability is $Cu^{2+} > Co^{2+} > Ni^{2+}$ which is not in agreement with the order given by, Irving and Williams[10]. The greater stability of Co(II) than Ni(II) may be attributed to the additional stabilization due to Jahn–

TABLE 1

PROTONATION CONSTANT OF THE LIGAND, METAL–LIGAND STABILITY CONSTANTS OF THE COMPLEXES, AND THERMODYANIC PARAMETERS AT THREE TEMPERATURES

Cation	*Constant*	*Temperature (°C)*			*—ΔG⁰ (kcal/mole)*			*ΔH⁰ (kcal/mole) at 30°C*	*ΔS⁰ (cal/mole/degree) at 30°C*
		20	*30*	*40*	*20°C*	*30°C*	*40°C*		
	$\log K_1H$*	5.57	5.37	5.27					
Cu^{2+}	$\log K_1$	2.98	2.90	2.87	3.99	4.02	4.11	−2.27	5.77
Ni^{2+}	$\log K_1$	2.82	2.80	2.78	3.78	3.88	3.98	−0.83	10.06
Co^{2+}	$\log K_1$	2.84	2.82	2.80	3.80	3.91	4.01	−0.83	10.16

* Carboxylic functional group.

Teller distortion present in case of Co(II). The value of log K_1 decreases with increase of temperature. The calculated error in stability constant is ± 0.01 log K.

The values of the overall changes in free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) accompanying complexation have been determined using the temperature coefficient and Gibbs–Helmholtz equation[11] (Table 1). The error in $\Delta G°$ and $\Delta H°$ values lies in the range 0.2–0.5 kcal/mole and that for $\Delta S°$ is 0.5 cal/degree mole. 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. Both enthalpy ($\Delta H°$) and entropy ($\Delta S°$) changes favour the formation of complexes.

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