Electrometric Study of Zn(II). Cd(II) and Hg(II) Complexes of DL-nor-Leucine

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COMPLEXATION equilibra of DL-nor-leucine [$CH_3.(CH_2)_2.CH(NH_2).COOH$] with zinc (II), Cadmium (II) and Mercury (II) has been determined by pH titration technique at 20°C, 30°C and 40°C and at ionic strength 0.1 M ($NaClO_4$) in aqueous medium. The formation curves reveal the formation of 1 : 1 and 1 : 2 complexes in each case and their stabilities determined by Calvin and Melchior's extension of Bjerrum method follow the order

$$Hg^{+2} > Zn^{+2} > Cd^{+2}$$

The overall changes in thermodynamic functions ΔG, ΔH and ΔS for the complexation reaction at 30°C have been determined with the help of an isobar and Gibb's Helmholtz equation.

AMINO-ACIDS, which constitute the unit structure of proteins, are directly involved in all the metabolic and enzymatic activities of every living being and have key role in nitrogen-assimilation. Several metel complexes of amino acids and their derivatives have already been reported by Saxena et al[1-4]. This communication deals with the study of the complexes formed between M^{+2} with DL-nor-leucine ($M^{+2} = Zn^{+2}$, Cd^{+2} and Hg^{+2}) the stability constants and overall changes in free energy, enthalpy and entropy, accompanying the complexation reactions.

EXPERIMENTAL

AnalaR grade reagents and B.D.H. poole's DL-nor-leucine (referred herein as HA) were used. The entire study was carried out in an inert atmosphere of nitrogen and fresh solutions were used to avoid any effects of ageing and air oxidation.

pH measurements were made on a Toshniwal digital pH-meter, with glass-calomel electrode assembly. A universal thermostat (U_2 type, German) was used to maintain the desired temperature.

pH titrations were carried out in presence and absence of metal ion against standard (0.1M) NaOH for establishing the stoichiometry of the complex formed during the interaction of metal ion and HA. For determining stability constants at 20°C, 30°C and 40°C, the ratio of metal to ligand was always one to five (1 : 5) and 6 mM $HClO_4$ is used for initial lowering of buffer region. The entire study was carried out in aqueous media at ionic strength of 0.1 M $NaClO_4$. Calvin and Melchior's extension of Bjerrum method was applied to calculate the stability constants of complexes formed.

RESULTS AND DISCUSSION

Stoichiometry : For establishing the stoichiometry of the complex species formed the magnitude of proton displacement was determined by titrating the solution containing metal ion and HA in different molar ratios against 0.1 M NaOH.

The addition of an equimolar concentration of metal ion greatly alters the shape of free ligand titiation curves (Fig. 1, curve 4) indicating the complex

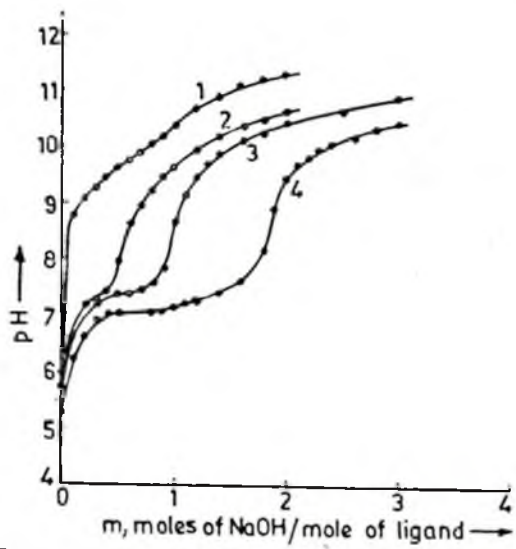


Fig 1 Potentiometeric titration of DL-nor-leucine in absence and presence of Zn^{++} with 0.1M NaOH
Curve (1) 4×10^{-3} M HA
Curve (2) 4×10^{-3} M HA + 1.0×10^{-3} M Zn^{++}
Curve (3) 4×10^{-3} M HA + 2.0×10^{-3} M Zn^{++}
Curve (4) 4×10^{-3} M HA + 4×10^{-3} M Zn^{++}

formation which results in the lowering of buffer region due to proton displacement

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

where M^{+n} stands for Zn^{+2}, Cd^{+2} and Hg^{+2}.

Since the extent of proton displacement depends on the relative affinity of the ligand for hydrogen ion and the metal ion, it is obvious from the curves (Fig. 1, curve 2,3,4) that the interaction of M^{+2} ion with HA is sufficient to compete with a relatively high concentration of hydrogen ion. The inflection at m = 2 (m being the moles of NaOH per mole of ligand) suggests the formation of either M(A)(OH) or $M(A)_2$ and $M(OH)_2$ in accordance with the following equations

$$M^{+2} + HA + 2\,OH^{-} \rightleftharpoons MA(OH) + HOH \quad (2)$$

$$M^{+2} + HA + 2\,OH^{-} \rightleftharpoons \tfrac{1}{2}\,M(A)_2 + \tfrac{1}{2}\,M(OH) + HOH \quad (3)$$

The appearance of precipitate during the titration rules out the possibility of formation of hydroxo-metal complex[5] and supports the formation of $M(A)_2$ and $M(OH)_2$. With the metal and the ligand in the ratio 1 : 2, the inflection is obtained at m = 1 (Fig. 1, Curve 3) which corresponds to the formation of $M(A)_2$. Since there in no significant inflection at m = 0.5, the formation of $M(A)^{+}$ and $M(A)_2$ must take place with considerable overlapping according to the following equations :

$$M^{+2} + HA + OH^{-} \rightleftharpoons M(A)^{+} + H_2O \quad (4)$$

$$M(A)^{+} + HA + OH^{-} \rightleftharpoons M(A)_2 + H_2O \quad (5)$$

$$M^{+2} + 2HA + 2OH^{-} \rightleftharpoons M(A)_2 + 2H_2O \quad (6)$$

i.e. 1 : 1, and 1 : 2 complexes are being formed simultaneously. The Inflection at m = 0.5 (Fig. 1 curve 2) confirms the above conclusions.

Stability constants : Calvin and Melchior's[6] extension of Bjerrum's[7] method has been employed for the determination of stability constants of the complexes.

The pH titrations of HA solution at ionic strength $\mu = 0.1$M ($NaClO_4$) and $HClO_4$ concentration (6mM) for initial lowering of buffer region in absence and presence of metal ions were carried out at 20°, 30° and 40°C against 0.1M NaOH and the concentration of the bound ligand, calculated from the horizontal distance between the corresponding curves, was divided by the total metal ion concentration to obtain the formation, function $\bar{n}$. At any pH, the value of free ligand concentration, [A], was calculated from the relations :

$$[A] = \frac{[HA]_{total} - [HA]_{bound}}{[H^{+}]/K_a + 1}$$

where K_a the dissociation constant[8] of HA, is 2.139×10^{-10}. 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 all the three metals Zn^{+2}, Cd^{+2} and Hg^{+2}. The overall stability constants of these metals follow the

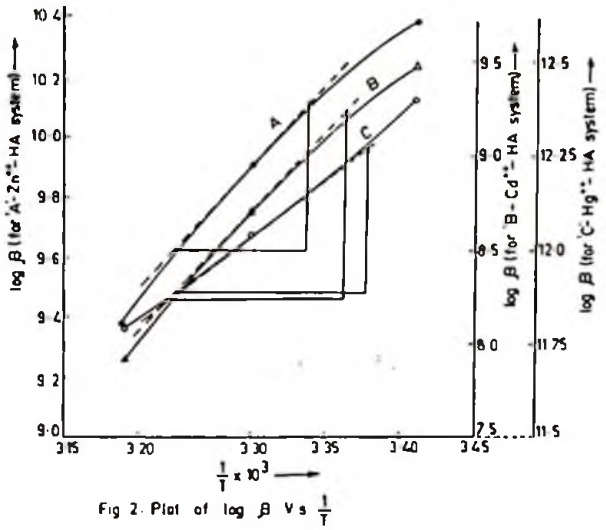


Fig 2. Plot of log β Vs $\frac{1}{T}$

order of $Hg^{+2} > Zn^{+2} > Cd^{+2}$, which can be explained by plotting a graph between log β and $(E_1 + E_2)$ (where E_1 and E_2 are the first and second ionization potentials) which resembles with the order given by A. Albert[9]. (Fig. 3).

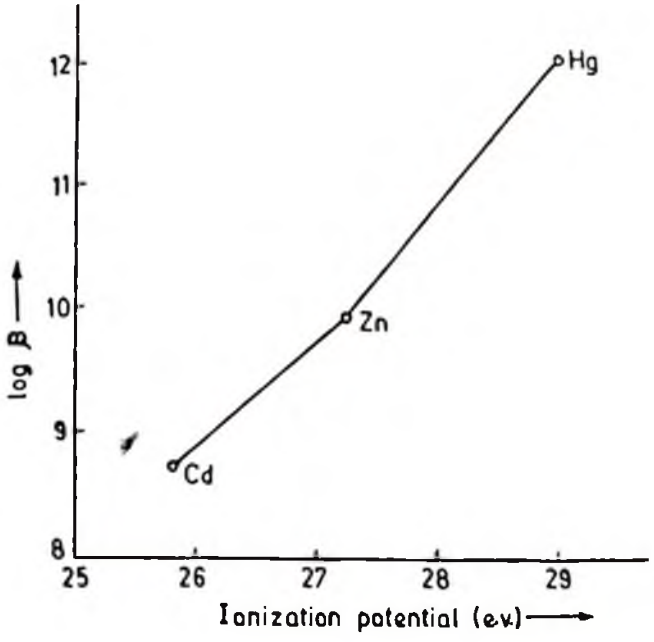


Fig. 3: Plot of log β vs Ionization potential (E_1+E_2)

Thermodynamic Functions : The values of overall changes in free energy (ΔG), enthalpy (ΔH)

and entropy (ΔS) accompanying complexation reactions have been determined at 30°C with the help of standard equations[10]. (Table II)

TABLE 1

Stepwise metal ligand stability constants of Zn(II), Cd(II) and Hg(II) complexes of DL-nor-leucine at different temperature ($\mu = 0.1$ M $NaClO_4$)

Constants	Values of stability constants at 20°C	30°C	40°C
Zn complexes			
log k_1	5.76	5.38	4.96
log k_2	4.62	4.53	4.42
log β	10.38	9.91	9.38
Cd complexes			
log k_1	5.49	5.02	4.49
log k_2	3.99	3.70	3.42
log β	9.48	8.72	7.91
Hg complexes			
log k_1	6.81	6.62	6.52
log k_2	5.59	5.42	5.27
log β	12.40	12.04	11.79

a Uncertainity limit = ±0.03

TABLE 2

Overall changes in thermodynamics functions for Zn (II), Cd(II) and Hg(II) complexes of DL-nor-leucine at 30°C

Metal Complex	ΔG (Kcals/mole)	ΔH (Kcals/mole)	ΔS (cal./deg/mole)
Zn(II)—complex	—13.74	—18.95	—17.19
Cd(II)—complex	—12.09	—20.04	—25.23
Hg(II)—complex	—16.68	—14.23	8.08

The values of ΔG is obtained from the expression

$$\Delta G = -RT \ln \beta$$

where β is the overall stability constant.
ΔH is determined with the help of an isobar

$$\frac{d(\log \beta)}{d(1/T)} = \frac{-\Delta H}{4.57}$$

The values of log β at different temperatures are plotted as a function of $\frac{1}{T}$. (Fig. 2).

The gradient of the tangent drawn at the point corresponding to 30°C is determined and equated to $\frac{-\Delta H}{4.57}$.

ΔS is than evaluated from the relation.

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

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