Studies in Complexation of Some Divalent Metal Ions with N-Benzoyl-Glycyl-L-Proline

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N-protected amino acids and peptides have been used as food supplements, herbicides, analgesics, inflammation inhibitors and antipyretics [1]. A lot of data on stability constants and thermodynamic parameters of different metal complexes with peptides is available in literature [2]. Sandhu and Rakesh Kumar [3] have reported the values of stability constants and thermodynamic parameters of Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Pb(II) with N-benzoyl-L-leucine and N-benzoyl-L-phenyl alanine. Log K values derived from polarographic data of Ruiz et al on Cd(II) with N-protected alanine - isoleucine mixed ligand system [4] are of similar order as reported by us. Investigating potentiometrically and using Irving-Rossotti technique on ligands possessing N, O, S donor atoms, Jaju and coworkers [5] have suggested certain geometrical forms of metal chelates. In this paper, the stability constants of complexes of Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Pb(II) with N-benzoyl-glycyl-L-proline in 50% V/V dioxane-water medium are reported at three different temperatures (25±0.1, 35±0.1 and 45±0.1). Overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) are derived.

EXPERIMENTAL

All chemicals used were of AnalaR (BDH) or equivalent grade. Dioxan was purified by recommended procedure [6]. N-benzoyl-glycyl-L-proline was prepared by the method reported in literature [7]. The potentiometric titration procedure for evaluation of apparent stability constants has been described earlier [3]. The method of Calvin-Bjerrum [8] as adopted by Irving and Rossotti [9] has been employed to determine the log K values.

RESULTS AND DISCUSSION

The respective metal ions in presence of the ligand were titrated against standard alkali. From shift in pH titration curves, values of $\bar{n}_H$, $\bar{n}$ and pL were calculated by Irving and Rossotti method [9]. The position of the ligand curve does not shift to left of the acid titration curve, in contrast to the observation in deprotected dipeptide systems. This indicates that benzoyl group which protected the amino group removed partially the possibility of zwitter ion formation in N-benzoyl-glycyl-L-

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proline. Thus only one protonation constant pK^{H}_{1} was obtained by various computational methods [8,10] and this is due to carboxylic group present in this ligand.

Likewise formation constants have been obtained by plotting $\bar{n}$ vs pL. The value of n, the average number of ligands attached per metal ion and free ligand component pL have been calculated by the Irving and Rossotti equations [9].

The value of $\bar{n}$ approaches 1 for the complexes of N-benzoyl-glycyl-L-proline with Cu(II), Ni(II), Co(II), Cu(II), Zn(II), Cd(II) and Pb(II) which suggests the formation of 1:1 complexes. The absence of 1:2 chelates may be due to steric hindrance offered to incoming second ligand molecule by coordinated ligand in 1:1 chelate. The Bjerrum half integral method [8] interpolation at various $\bar{n}$ values and graphical method [10] as extended to dioxan-water mixture by Van Uitert and Haas [11] have been used to calculate the log K_1 values.

The values of log K_1 have also been determined at three different concentrations of metal ion (keeping ligand concentration constant) to show that only mononuclear complexes are formed. The mean values of concentration stability constants (log K_1) are summarized in Table 1. These values are comparable with those reported for acetates which suggests that the formation of the complexes occurs by interaction of the carboxylate group of N-benzoyl-glycyl-L-proline. The order of stability is Pb(II) > Cu(II) > Zn(II) > Co(II) > Ni (II) > Cd[II). The greater stability of Co(II) than Ni(II) complexes may be attributed to the additional stabilisation due to Jahn-Teller distortion present in case of Co(II) similar to Cu(II) and to favourable entropy effect, while partial oxidation of the Co(II) complexes is not absolutely ruled out. The values of log K_1 increase in general with increase of temperature.

Table 1

Values of Protonation Constant, Stability Constants and Thermodynamic function of Complexes

Ligand: N-benzoyl-glycyl-L-proline anion

Metal ion	<— log K_1 at —> 25°C	35°C	45°C	<— ΔG° at —> 25°C	35°C	45°C	ΔH° 35°C	ΔS° 35°C
H*	4.90	4.80	4.70					
Cu(II)	2.89	2.97	3.02	3.94	4.19	4.39	2.80	22.69
Co(II)	2.78	2.80	2.84	3.79	3.95	4.13	1.31	17.08
Ni(II)	2.71	2.75	2.81	3.69	3.88	4.09	2.18	19.67
Zn(II)	2.82	2.85	2.87	3.85	4.02	4.18	1.08	16.57
Cd(II)	2.69	2.76	2.80	3.69	3.89	4.07	2.36	20.29
Pb(II)	3.02	3.02	3.06	4.12	4.26	4.45	1.79	19.64

* G and H in k.cal/mole; S in cal/mole/degree

The values of overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying complexation have been determined using the temperature coefficient and Gibb's Helmholtz equation [12] (Table 1). The error in ΔG and ΔH values lies in the range 0.2 to 0.5 k cal/mole and that for ΔS is 0.5 cal/

degree/ mole. The free energies of formation (ΔG) of the complexes have more negative values with increase of temperature, showing that complex formation is a spontaneous process. Both enthalpy (ΔH) and entropy (ΔS) changes favour formation of complexes.

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