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Note

Complexation reaction of metal ions with peptide systems. Part IV. A potentiometric study of rare earth complexes of glycyl-L-proline

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Amino acids and dipeptides are of biological importance and therefore their metal complexes are of special interest. Many workers have studied the complexes of various peptides with different transition metals in solution[1–5]. Although the stability of complexes of lanthanum with amino acids has been studied[6–11], no work appears to have been done with dipeptide systems. In continuation to our previous work[12, 13] on the complexation reactions of lanthanides with dipeptide systems, the present communication reports the stability constants and thermodynamic functions of Y(III), La(III), Ce(III), Pr(III) and Nd(III) with glycyl-L-proline in aqueous medium at 25, 35 and 45°C at 0.15 M (KNO_3) ionic strength. The Calvin–Bjerrum titration technique[14, 15] as modified by Irving and Rossotti[16] was used.

EXPERIMENTAL

Metal nitrates were prepared by the action of nitric acid on the corresponding AnalaR grade metal oxides and their purity was checked by EDTA titration. Stock solution of (0.005 M) metal nitrates were prepared in double distilled water.

The ligand glycyl-L-proline was obtained from Koch-Light laboratories and was dried at 100°C for 24 h. Fresh ligand solution (0.025 M) was prepared just before use in double-distilled water.

Carbonate-free potassium hydroxide (0.0526 M) solution was prepared by Vogel's method[17].

Nitric acid (0.0051 M), potassium hydrogen phthalate (0.05 M), potassium nitrate (1 M) and borax (0.01 M), all of B.D.H. AnalaR grade, were prepared in double-distilled water.

The pH was measured on a photovolt digicord pH meter having a sensitivity of ±0.002. The pH meter was calibrated with potassium hydrogen phthalate and

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N CONSTANT OF THE LIGAND, METAL–LIGAND STABILITY CONSTANTS OF THE COMPLEXES AND THERMODYNAMIC PARAMETERS AT THREE TEMPE

Protonation constant/metal ligand stability constants	*Temperature*			*$-\Delta G$(kcal mole^{-1})*			*ΔH(kcal mole^{-1})*	*ΔS(cal mole^{-}*
	25°C	*35°C*	*45°C*	*25°C*	*35°C*	*45°C*	*at 35°C*	*at 35°C*
$\log {}^{P}K_{1}^{H}$	8.55	8.40	8.23					
$\log K_1$	3.80	3.90	4.04	5.17	5.49	5.87	5.23	34.77
$\log K_1$	3.46	3.56	3.66	4.71	5.00	5.31	4.34	30.33
$\log K_1$	3.50	3.60	3.73	4.76	5.06	5.42	5.00	33.07
$\log K_1$	3.59	3.67	3.81	4.88	5.16	5.53	4.81	32.29
$\log K_1$	3.65	3.76	3.90	4.97	5.29	5.66	5.44	38.43

borax buffers. All titrations were carried out in a thermostated bath maintained at temperatures 25 ± 0.1, 35 ± 0.1 and 45 ± 0.1 °C.

The details of procedure and calculations of $\bar{n}$, pL and thermodynamic functions are described elsewhere[10].

RESULTS AND DISCUSSION

The practical proton–ligand and metal–ligand stability constants and thermodynamic functions are summarized in Table 1. The mole ratio of metal to glycyl-L-proline was kept at 1:5 in order to fulfil the maximum co-ordination number of the metal ion. In the initial stages of titration, the ligand titration curve was above the acid titration curve due to the acceptance of a proton by the amino group from the strongly acidic medium. The neutralization of the –COOH group of the zwitter ion is completed where the ligand curve crosses the acid curve. The further course of the ligand curve is due to neutralization of a second proton from the ligand. The other curves were of usual shape.

The mean values of $\log {}^{\mathrm{P}}K_1^{\mathrm{H}}$ at 25, 35 and 45 °C are 8.55, 8.40 and 8.23, respectively. The value of $\log {}^{\mathrm{P}}K_1^{\mathrm{H}} = 8.55$ at 25 °C is within the error limits (±0.05) of the value reported in the literature[2, 5]. The value of $\log {}^{\mathrm{P}}K_1^{\mathrm{H}}$ decreases with increase in temperature.

The formation curve for the metal–ligand complex was obtained by plotting $\bar{n}$ versus pL. The value of $\bar{n}$ was calculated below the pH range at which precipitation occurs. The precipitation of Y(III), La(III), Ce(III), Pr(III) and Nd(III) complexes was observed at pH 7.75, 7.6, 7.6, 7.5 and 7.45, respectively, at 35 °C. The precipitation takes place at lower pH with increase in temperature.

The values of $\bar{n}$ obtained indicate the formation of 1:1 complexes of Y(III), La(III), Ce(III), Pr(III) and Nd(III) with glycyl-L-proline. Since the values of $\log K_1$ increases with rise in temperature, so a higher temperature is favourable for the formation of complexes. The overall stability at these temperatures is Y(III) > Nd(III) > Pr(III) > Ce(III) > La(III) as expected on the basis of the ionic radii of the metal ions.

The values of ΔH show that reactions of these metals with glycyl-L-proline are endothermic. Since the complex formation reaction is favoured by higher temperature, so the value of $\log K_1$ increases with temperature. In all the systems the entropy change is positive and favours complex formation. The value of free energies of formation become more negative with increase in temperature which indicate that the complex formation becomes more spontaneous with temperature.

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