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Note

COMPLEXATION REACTION OF METAL IONS WITH PEPTIDE SYSTEMS. PART XIII. STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF PRASEODYMIUM(III), NEODYMIUM(III) AND SAMARIUM(III) WITH L-TYROSYLGLYCYLGLYCINE AND L-LEUCYLGLYCYLGLYCINE

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The capacity of amino acids and peptides to form metal complexes is of theoretical and practical significance in understanding the biological action of these metal ions. Though there is considerable information about formation constants of metal complexes of amino acids [1,2] with rare earths, little work appears to have been reported for complexes of tripeptides [3]. The present paper deals with the study of complexes of L-tyrosylglycylglycine and L-leucylglycylglycine with Pr^{3+}, Nd^{3+} and Sm^{3+} in aqueous solution at 0.1 M ionic strength (KNO_3) and at three different temperatures (25, 35 and 45°C). The parameters have been calculated by the Calvin—Bjerrum titration technique [4,5] as modified by Irving and Rossotti [6].

EXPERIMENTAL

All chemicals used were of BDH Analar quality. L-Tyrosylglycylglycine and L-leucylglycylglycine were obtained from Fluka Chemicals. Doubly-distilled carbon dioxide-free water was used in all experimental work. The metal nitrate solutions were standardized by EDTA method. Fresh ligand solutions (0.025 M) were prepared just before use. pH was measured on a Toshniwal CL 46 pH meter having a sensitivity of ±0.01 units. The pH meter was calibrated using suitable buffers. All titrations were carried out in a thermostated bath maintained at constant temperatures of 25 ± 0.1, 35 ± 0.1 and 45 ± 0.1°C. The following sets of solutions were titrated against a standard solution (0.05 M) of carbonate-free potassium hydroxide.

(a) Acid titration: nitric acid (0.005 M, 5 ml)

(b) Reagent titration: nitric acid (0.005 M, 5 ml) + reagent (0.025 M, 5 ml).

(c) Metal titration: nitric acid (0.005 M, 5 ml) + reagent (0.025 M, 5 ml) + metal nitrate (0.005 M, 5 ml).

In all the titrations the total volume of solution was kept to 50 ml and the required amount of potassium nitrate solution (1.0 M) was added to bring the ionic background to the required level (0.1 M). Nitrogen gas was bubbled through the solution to provide the inert atmosphere. The concentrations were corrected for the changes in volume produced by the addition of alkali during titration.

RESULTS AND DISCUSSION

It was observed in both the ligands that in the initial stages of titration the ligand titration curves were above the acid titration curves due to the acceptance of a proton by the amino group from the strongly acidic media. The neutralization of the —COOH group of the Zwitterion is completed where the ligand titration curve crosses the acid titration curve. The further course of the ligand curve is due to the neutralization of a second proton from the ligand.

$\bar{n}_H$, $\bar{n}$ and pL were calculated by employing the relationships derived by Irving and Rossotti [7]. The proton—ligand formation curves were obtained by plotting the degree of formation ($\bar{n}_H$) of the proton complex against the pH value. The practical proton—ligand stability constant, log pK_1^H, was obtained by the Bjerrum half-integral method and graphical method [5—7]. The value of log pK_2^H was obtained using the relationship

$$\log \mathrm{p}K_1^H \mathrm{p}K_2^H = 2\ \mathrm{pH}\ (\text{at } \bar{n}_H = 1)$$

The values of log pK_1^H and log pK_2^H for both the ligands at 25, 35 and 45°C are shown in Tables 1 and 2. The data show a decrease in the values of log pK_1^H and log pK_2^H with increase in temperature.

The metal—ligand formation curves were obtained by plotting $\bar{n}$ vs. pL. The metal—ligand stability constants were determined by the Bjerrum half-integral method, point-wise calculations and graphical methods [5—7]. The values of log K_1 obtained by different methods agree fairly well and their average values are summarized in Tables 1 and 2. The values of $\bar{n}$ obtained indicate the formation of 1 : 1 complexes of Pr^{3+}, Nd^{3+} and Sm^{3+} with L-tyrosylglycylglycine and L-leucylglycylglycine below the pH range at

TABLE 1

Protonation constants of L-tyrosylglycylglycine, metal—ligand stability constants of the complexes and thermodynamic parameters at three temperatures (μ = 0.1 M)

Metal ion	Protonation constant/ metal—ligand stability constant	Temp. (°C)			—ΔG (kcal mole^{-1})			ΔH (kcal mole^{-1}) at 35°C	ΔS (cal mole^{-1} deg^{-1}) at 35°C
		25	35	45	25	35	45		
H^+	log pK_1^H	7.76	7.40	7.20					
	log pK_2^H	3.44	2 60	2.20					
Pr^{3+}	log K_1	3.45	3.49	3.51	4.70	4.92	5.11	1.29	20.00
Nd^{3+}	log K_1	3.55	3.65	3.68	4.84	5.14	5.36	2.77	25.68
Sm^{3+}	log K_1	3.60	3.72	3.76	4.91	5.24	5.47	3.42	28.12

TABLE 2

Protonation constants of L-leucylglycylglycine, metal—ligand stability constants of the complexes and thermodynamic parameters at three temperatures (μ = 0.1 M)

Metal ion	Protonation constant/ metal—ligand stability constant	Temp. (°C)			$-\Delta G$ (kcal mole^{-1})			ΔH (kcal mole^{-1}) at 35°C	ΔS (cal mole^{-1} deg^{-1}) at 35°C
		25	35	45	25	35	45		
H^+	log pK_1^H	7.82	7.57	7.10					
	log pK_2^H	3.18	3.13	3.10					
Pr^{3+}	log K_1	3.23	3.24	3.26	4.40	4.57	4.74	0.66	16.98
Nd^{3+}	log K_1	3.27	3.29	3.33	4.46	4.64	4.85	1.32	19.35
Sm^{3+}	log K_1	3.44	3.46	3.48	4.69	4.88	5.06	0.87	18.67

which precipitation occurred. The data show in both cases an increase in the values of log K_1 with increase in temperature. This shows that higher temperatures are favourable for the complex formation. The overall order of stability in both cases at the three temperatures is $Sm^{3+} > Nd^{3+} > Pr^{3+}$, as expected on the basis of their electronic configurations.

The values of overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) have been determined using the temperature coefficient and Gibb's—Helmholtz equation [8] and are summarized in Tables 1 and 2 for the complexes of L-tyrosylglycylglycine and L-leucylglycylglycine.

For all the metals the change in free energy value becomes more negative with increase in temperature. This shows that the complex formation process is spontaneous and the spontaneity increases with increase in temperature. The values of enthalpy change in all the cases are positive, which explains the increase in the values of formation constants with rise in temperature. But the positive values of ΔS in all cases indicate that the complex formation is favoured by increase in entropy of the system.

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