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Note

COMPLEXATION REACTION OF METAL IONS WITH PEPTIDE SYSTEMS. PART XIV. A POTENTIOMETRIC STUDY OF RARE EARTH COMPLEXES OF L-LEUCYLGLYCYLGLYCINE

RANJIT SINGH SANDHU and RAKESH KUMAR

Department of Chemistry, Guru Nanak Dev University, Amritsar 143005 (India)

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Amino acids and peptides are of biological importance and therefore their metal complexes are of special interest. The complexation reactions of a number of peptides with transition metals have been reported in the literature [1,2], but little work appears to have been done with rare earth metal ions [3,4]. In the present study, the stability constants of complexes of La^{3+}, Ce^{3+}, Gd^{3+}, Er^{3+}, Dy^{3+}, Yb^{3+} and Y^{3+} with L-leucylglycylglycine have been determined in aqueous medium at 0.1 M ionic strength (KNO_3) and at three different temperatures (25, 35 and 45°C) using the titration technique of Irving and Rossotti [5]. The thermodynamic functions (ΔG, ΔH, and ΔS) are reported.

EXPERIMENTAL

Metal nitrates were prepared from the corresponding Analar grade oxides and their purity checked before use. The ligand was obtained from Fluka chemicals. All solutions were prepared in doubly distilled carbon dioxide-free water. The metal nitrate solutions were standardized by EDTA method. The fresh ligand solution (0.025 M) was prepared just before use. The pH was measured on a Toshniwal pH meter CL 46 having a sensitivity of ±0.01 units. The pH meter was calibrated by suitable buffers. All titrations were carried out in a thermostated bath maintained at temperatures of 25 ± 0.1, 35 ± 0.1 and 45 ± 0.1°C. The three solutions (total volume 50 ml in each case) were prepared as follows:

(A) 5 ml of 0.005 M HNO_3;
(B) 5 ml of 0.005 M HNO_3 + 5 ml of 0.025 M ligand;
(C) 5 ml of 0.005 M HNO_3 + 5 ml of 0.025 M ligand + 5 ml of 0.005 M metal nitrate.

An appropriate quantity of potassium nitrate solution (1.0 M) was added to maintain the desired ionic strength of 0.1 M. The above solutions were titrated against standard potassium hydroxide solution.

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TABLE 1

Protonation constants of L-leucylglycylglycine, metal—ligand stability constants of the complexes and thermodynamic parameters at three temperatures and $\mu = 0.1$ M

Cation	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°C	35°C	45°C		
H^+	pK_1^H	7.82	7.57	7.10					
	pK_2^H	3.18	3.13	3.10					
La^{3+}	$\log K_1$	3.13	3.20	3.22	4.27	4.51	4.69	1.92	20.88
Ce^{3+}	$\log K_1$	3.21	3.22	3.24	4.38	4.54	4.71	0.66	16.88
Gd^{3+}	$\log K_1$	3.36	3.38	3.41	4.58	4.76	4.96	1.14	19.15
Dy^{3+}	$\log K_1$	3.47	3.51	3.54	4.73	4.95	5.15	1.51	20.97
Er^{3+}	$\log K_1$	3.49	3.54	3.58	4.76	4.99	5.21	1.95	20.53
Yb^{3+}	$\log K_1$	3.68	3.70	3.72	5.02	5.21	5.41	0.87	19.74
Y^{3+}	$\log K_1$	3.30	3.33	3.36	4.50	4.69	4.89	1.30	19.45

RESULTS AND DISCUSSION

$\bar{n}_H$, $\bar{n}$ and pL were calculated by employing the relationship derived by Irving and Rossotti [5]. The practical proton—ligand stability constants and the metal—ligand stability constants were obtained by the Bjerrum half-integral method [6] and also by graphical method [7]. The results are given in Table 1.

The values of $\bar{n}$ obtained are of the order of 1, indicating the formation of 1 : 1 complexes of La^{3+}, Ce^{3+}, Gd^{3+}, Dy^{3+}, Er^{3+}, Yb^{3+} and Y^{3+} with L-leucylglycylglycine below the pH range at which precipitation occurred. The data in Table 1 show an increase in the value of $\log K_1$ with increase in temperature. The order of stability is $Y^{3+} > La^{3+} < Ce^{3+} < Gd^{3+} < Dy^{3+} < Er^{3+} < Yb^{3+}$.

The values of overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were determined by using the temperature coefficient and the Gibbs—Helmholtz equation. The results are summarized in Table 1. The values of free energy of formation become more negative with increase in temperature. This shows that the complex formation process is spontaneous and spontaneity increases with increase in temperature. The results in Table 1 show low positive values of ΔH, but high ΔS values, thus indicating that the rare earth L-leucylglycylglycinate chelates are entropy stabilized. This is because in aqueous solution, complexation by chelation is favoured by the release of bonded water molecules [8].

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