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Note

Complexation reaction of metal ions with peptide systems. Part II. Potentiometric studies of the complexes of glycyl-DL-valine with Gd^{3+}, Dy^{3+}, Er^{3+} and Yb^{3+}

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The stable complexes of amino acids with rare earths have found importance in the separation of these metals[1]. The complexation reactions of a number of dipeptides with copper and nickel have been reported in the literature[2–9]; but little work appears to have been done with rare earth metals. This paper is a continuation of our earlier communication[10], and deals with the study of complexes of Gd^{3+}, Dy^{3+}, Er^{3+} and Yb^{3+} with Glycyl-DL-valine. The Calvin–Bjerrum[11, 12] pH titration technique, as modified by Irving and Rossotti[13], has been employed.

EXPERIMENTAL

Metal nitrates were prepared from the corresponding oxides of analar grade and their purity checked before use. The ligand was obtained from Koch-Light Laboratories Ltd., London. 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. Potassium nitrate (1.0 M) was used to maintain constant ionic strength of 0.15 M. The pH was measured on a photovolt digicord pH meter having a sensitivity of ±0.002. The pH meter was calibrated by suitable buffers. All titrations were carried out in a thermostat bath maintained at temperatures 25 ± 0.1 °C, 35 ± 0.1 °C and 45 ± 0.1 °C. The following sets of solutions were titrated against a standard solution of 0.050 M potassium hydroxide free of carbon dioxide.

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 titrations the total volume of solution was kept at 50 ml and the required amount of potassium nitrate solution (1.0 M) was added to bring the ionic background

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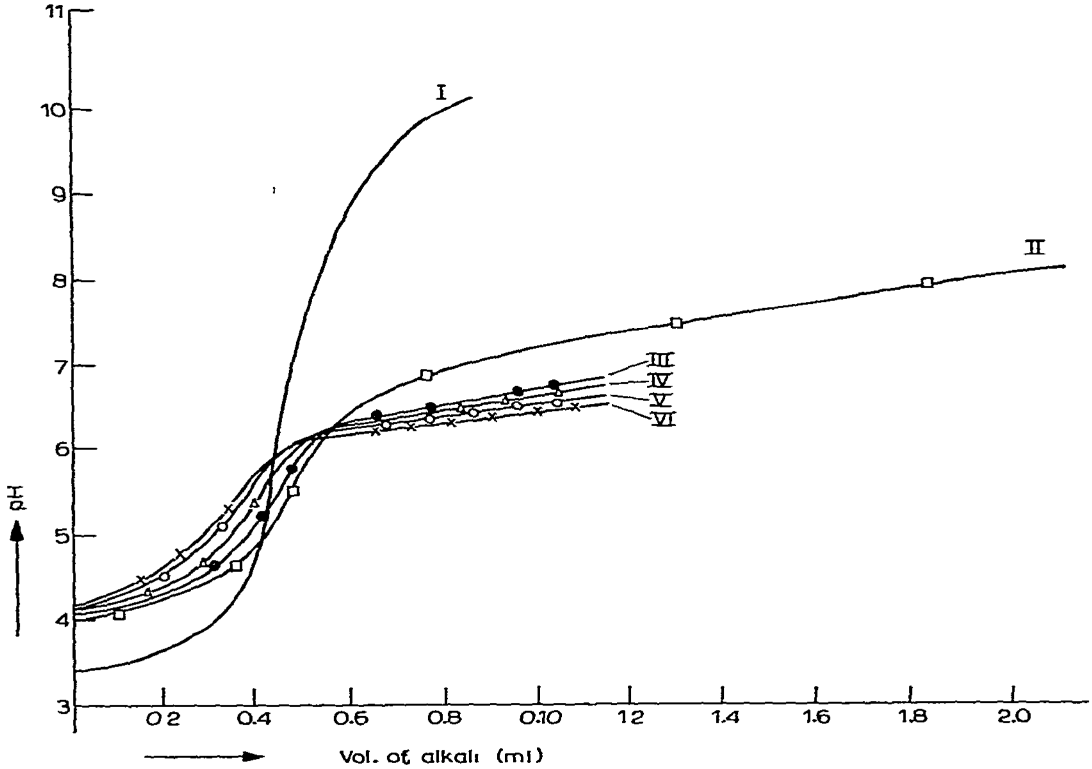
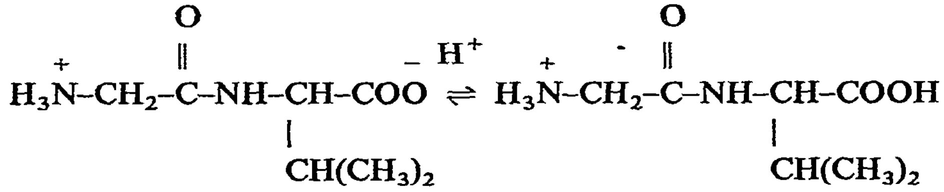


Fig. 1. I, acid; II, acid + ligand; III, acid + ligand + Gd^{3+}; IV, acid + ligand + Dy^{3+}; V, acid + ligand + Er^{3+}; VI, acid + ligand + Yb^{3+}.

to the required level. Nitrogen gas was bubbled through the solution to provide an inert atmosphere. The concentrations were corrected for the changes in volume produced by the addition of alkali during titration. The calculated error in stability constants is ± 0.01 log K units.

RESULTS AND DISCUSSION

From the shift in pH titration curves (Fig. 1) values of $\bar{n}_A$, $\bar{n}$ and pL were calculated by employing the relationships derived by Irving and Rossotti[13]. It was noted that the ligand curve (II) is slightly shifted to the left of the acid titration curve (I) at lower pH values. The shift is due to interaction of the Zwitterion and the proton.



$$\overset{+}{H_3N}\text{-}CH_2\text{-}\underset{}{\overset{\overset{\displaystyle O}{\|}}{C}}\text{-}NH\text{-}\underset{\underset{\displaystyle CH(CH_3)_2}{|}}{CH}\text{-}CO\overset{-}{O} \overset{H^+}{\rightleftharpoons} \overset{+}{H_3N}\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NH\text{-}\underset{\underset{\displaystyle CH(CH_3)_2}{|}}{CH}\text{-}COOH$$

The neutralization of the –COOH group of the Zwitterion is completed where curve (II) crosses curve (I). The onward course followed by curve (II) is due to the neutralization of a second proton from the ligand.

TABLE 1

PROTONATION CONSTANT OF THE LIGAND, METAL–LIGAND STABILITY CONSTANTS OF THE COMPLEXES AND THERMODYNAMIC PARAMETERS AT THREE TEMPERATURES

Metal ions	*Protonation constant/ metal–ligand stability constants*	*Temperature (°C)*			*$-\Delta G$(kcal mole^{-1})*			*ΔH(kcal mole^{-1})*	*ΔS(cal mole^{-1} deg^{-1})*
		25	*35*	*45*	*25°C*	*35°C*	*45°C*	*35°C*	*35°C*
	log $^{P}K_{1}^{H}$	8.32	8.13	7.95					
	log $^{P}K_{2}^{H}$	3.42	2.73	2.05					
Gd^{3+}	log K_1	3.87	3.95	4.03	5.270	5.560	5.856	3.468	29.31
Dy^{3+}	log K_1	3.98	4.04	4.08	5.420	5.687	5.929	2.154	25.46
Er^{3+}	log K_1	4.04	4.09	4.13	5.506	5.757	5.908	1.944	25.00
Yb^{3+}	log K_1	4.08	4.13	4.17	5.556	5.819	6.059	1.944	25.98

The proton–ligand formation curve was obtained by plotting the degree of formation ($\bar{n}_A$) of the proton complex against the pH value. The practical proton–ligand stability constant ($\log^{P}K_1^{H}$) has been obtained by the Bjerrum half-integral method and graphical method[12, 13]. The value of $\log^{P}K_2^{H}$ was obtained by using the following relationship:

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

The values of $\log^{P}K_1^{H}$ and $\log^{P}K_2^{H}$ at 25, 35 and 45°C are 8.32, 3.42; 8.13, 2.73; 7.95, 2.05, respectively. The values are close to those reported by Petrov et al.,[6] at 25°C. The data show a decrease in the values of $\log^{P}K_1^{H}$ and $\log^{P}K_2^{H}$ with increase in temperature.

The metal curves (III–VI) also shift a little to the left of the ligand curve. This may be due to ionic interaction of the metal ion and the carboxylate group of the ligand which results in the formation of a stronger Zwitterion. The metal–ligand formation curve was obtained by plotting $\bar{n}$ vs. pL. Metal–ligand stability constants were determined by the Bjerrum half-integral method, pointwise calculations and graphical methods[12, 13] by using the equation $\log K_1 = \mathrm{pL} - \log(1 - \bar{n})/\bar{n}$. The values of $\log K_1$ obtained by different methods agree fairly well and their average values are summarized in Table 1. The values of $\bar{n}$ obtained indicate the formation of 1:1 complexes of Gd^{3+}, Dy^{3+}, Er^{3+} and Yb^{3+} with Glycyl-DL-valine below the pH range at which precipitation occurred. The data as given in Table 1 shows an increase in the value of $\log K_1$ with increase in temperature. This shows that higher temperature is favourable for the formation of complexes. The overall order of stability at the three temperatures is $Yb^{3+} > Er^{3+} > Dy^{3+} > Gd^{3+}$, 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 by using the temperature coefficient and the Gibbs–

Helmholtz equation. The values are summarized in Table 1. 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 cases are positive and this 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.

The chelation of peptide to metal ion appears to be through terminal nitrogen and peptide oxygen, as reported in the case of copper complexes with dipeptides [2, 5, 9, 14, 15].

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