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A THERMODYNAMIC STUDY OF THE COMPLEXATION REACTION FOR SOME AMINO ACIDS WITH CERIUM(III) AND YTTRIUM(III)

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ABSTRACT

The thermodynamic parameters for the complexation reaction of leucine, valine, proline and hydroxyproline with cerium(III) and yttrium(III) were determined potentiometrically in aqueous solution at 25, 35 °C and $\mu = 0.1$. The values for the formation constants have been reported. The values of enthalpy changes (ΔH) and entropy changes (ΔS) are positive for all systems. The chelation effect is believed to be essentially an entropy effect.

INTRODUCTION

A study of metal–amino acid complexes is of immense importance from a biological standpoint as it is likely to contribute to a better understanding of the linkage involved in metal–protein interactions. Though there is considerable information about formation constants of co-ordination complexes of amino acids in aqueous solution, very little data are available in literature on the enthalpies and entropies of complex formation of cerium(III) and yttrium(III) with the amino acids. A study has been initiated in this laboratory on the thermodynamics of interaction of such metal ions with amino acids in aqueous solutions. For such systems, the formation constant data is available for complexes of cerium(III) and yttrium(III) with threonine, methionine, lysine and arginine[1].

Rogozina *et al.*[2] reported the complex formation of cerium(III) with tryptophan, histidine and phenylalanine in aqueous solutions. In the present paper are reported the formation constants, enthalpy changes (ΔH) and entropy changes (ΔS) associated with formation of complexes of leucine, valine, proline and hydroxyproline with cerium(III) and yttrium(III).

EXPERIMENTAL

Materials

Standard carbonate-free potassium hydroxide[3] was used for the potentiometric titrations. Hydrochloric acid was prepared from Analar (BDH) grade acid. All inorganic salts were of Analar grade. The solution of Y^{III} was prepared by dissolving its nitrate (BDH) in doubly distilled water and estimated as usual[4]. $Ce_2(SO_4)_3$·

$8H_2O$ (BDH) was used for preparing the solution. The amino acids, D,L-leucine, D,L-valine, L-proline and L-hydroxyproline were obtained from Merck Laboratories, Germany. All the amino acids were used after drying for 24 h at 100°C. All the solutions were prepared in doubly distilled water. The pH was measured by a systronic pH meter using glass and calomel electrodes. The measurements were checked before and after the titration with standard buffers. The titrations were carried out at 25 $\pm$0.1 and 35 $\pm$0.1 °C in a constant temperature water bath.

Procedure

The mole ratio of metal to ligand was kept 1:5 in order to fulfil the maximum co-ordination number of metal ion. The following solutions (total volume 20 ml) were titrated against standard alkali by pH-titration method: (A) 2.00 ml of HCl (0.005 M); (B) A + 2 ml of ligand (0.05 M); and (C) B + 2 ml of metal (0.01 M).

An ionic strength of 0.1 was established by addition of a calculated amount of potassium chloride. The plots of pH against the volume of alkali required to obtain the corresponding pH change were plotted. The shapes of titration curves were obtained as usual.

In order to determine the protonation constants and successive formation constants, the Calvin–Bjerrum[5,6] pH-titration technique as adopted by Irving and Rossotti[7] was used. The protonation constants and formation constants were calculated on the basis of a formation function, applying the least-squares principle[8].

RESULTS AND DISCUSSION

The formation curves of cerium(III) and yttrium(III) complexes may be seen in Figs. 1–4. The $\bar{n}$ values for complexes of cerium indicate the formation of 1:1 complexes in pH range 6.00–7.50. The $\bar{n}$ values for complexes of yttrium(III) show that they are greater than 1 and less than 2, indicating the formation of 1:1 and 1:2 com-

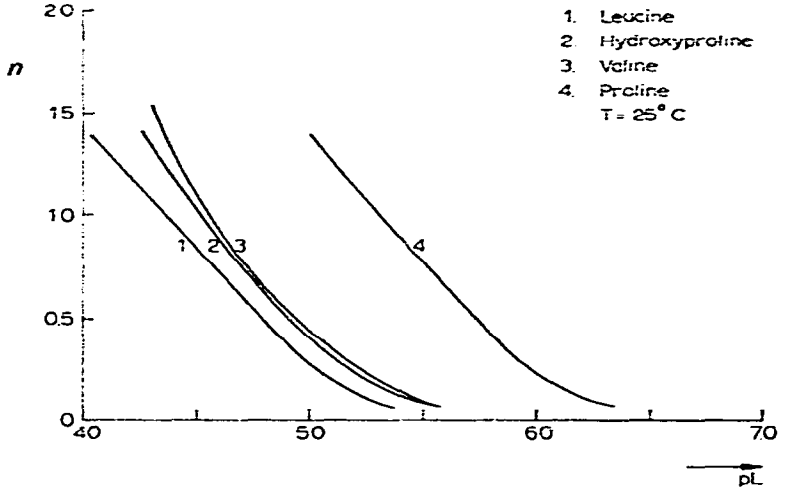

Fig. 1. Formation curves for Y^{III}–amino acid systems.

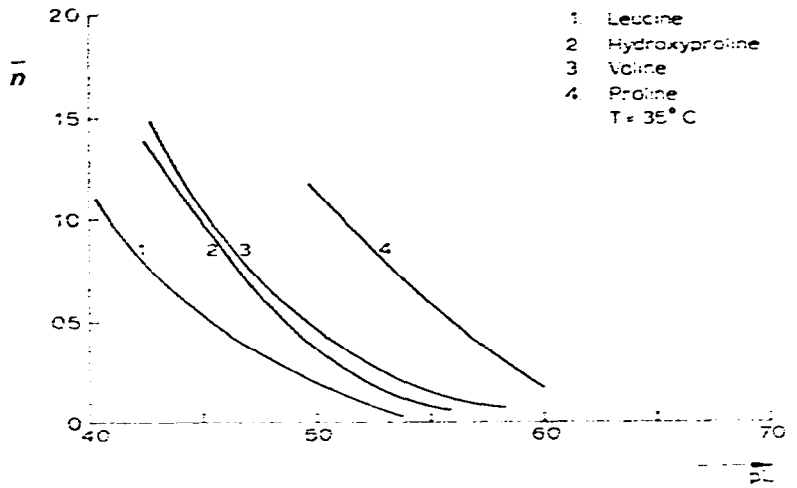

Fig. 2. Formation curves for Y^{III}–amino acid systems.

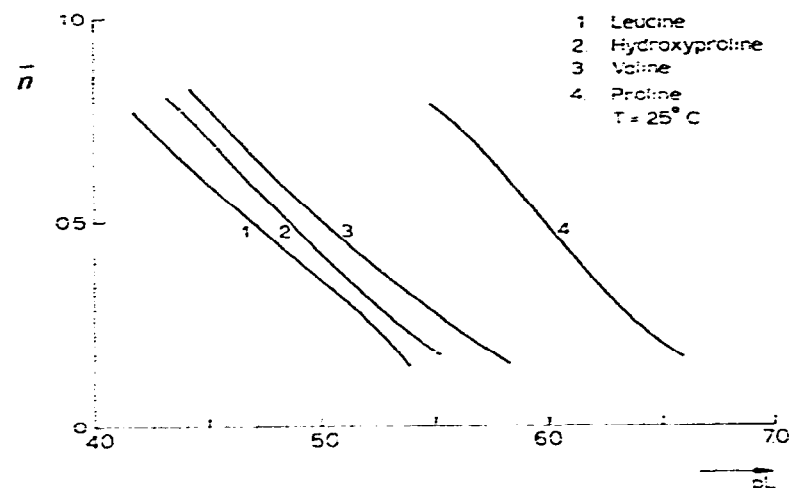

Fig. 3. Formation curves for Ce^{III}–amino acid systems.

plexes in pH range 6.00–7.75. From the metal titration curves, precipitation was observed in the cases of cerium and yttrium above pH 7.50 and 7.75 respectively.

The values of protonation constants of the ligands and the successive formation constants for various systems are given in Tables 1 and 2. The following relationships were used to derive the thermodynamic parameters

$$\Delta G = -RT \ln K$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\Delta G = \Delta H - T\Delta S$$

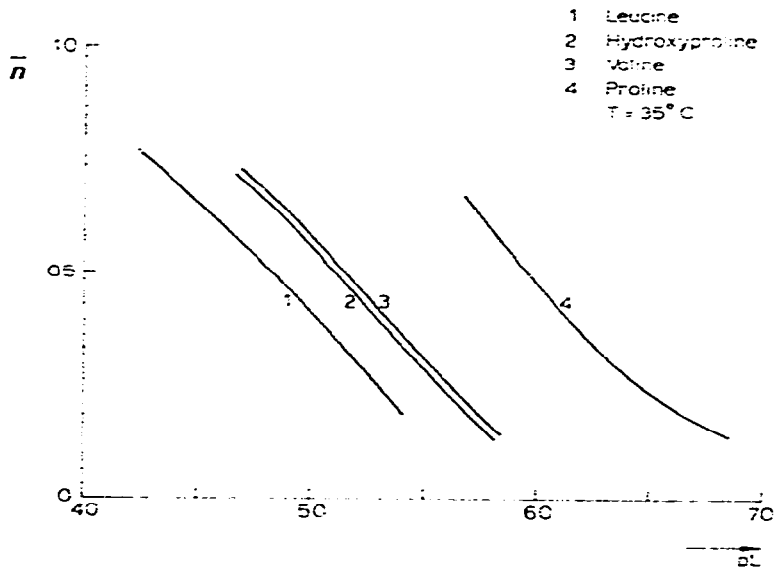

Fig. 4. Formation curves for Ce^{III}–amino acid systems.

TABLE I

PROTONATION CONSTANTS OF AMINO ACIDS ($\mu = 0.1$ M)

Amino acid	*T* (°C)	pK_1	pK_2
leucine	25	2.33	9.60
	35	2.18	9.35
valine	25	2.30	9.80
	35	2.22	9.56
proline	25	1.95	10.55
	35	1.85	10.30
hydroxyproline	25	1.82	9.70
	35	1.75	9.55

The values of free energy of formation (ΔG), enthalpy changes (ΔH) and entropy changes (ΔS) are summarized in Tables 3–5. Values of formation constants are accurate to ± 0.05 log units and derived ΔH values are accurate to ± 0.6 kcal mole^{-1}.

The values of log K_1/K_2 are positive in all cases (Table 2). Similar results have been reported in literature and have been explained due to combination of factors, such as statistics, steric hindrance and for charged ligands due to coulombic interactions. In comparing the complex-formation properties of proline and hydroxyproline, we observed that more stable complexes are formed in the interaction of cerium and yttrium with proline. Thus the introduction of –OH group reduces the stability of complexes which is in accordance with Perkins findings[9]. Valine forms more stable

TABLE 2
FORMATION CONSTANTS OF METAL COMPLEXES OF AMINO ACIDS

Amino acid	*T* (°C)	Y^{III}			Ce^{III}
		$\log K_1$	$\log K_2$	$\log \beta_2$	$\log K_1$
leucine	25	4.26	3.90	8.16	4.69
	35	4.45	4.20	8.65	4.92
valine	25	4.79	4.27	9.06	5.02
	35	4.59	4.48	9.07	5.22
proline	25	5.40	4.81	10.21	6.00
	35	5.55	5.05	10.60	6.08
hydroxyproline	25	4.52	4.40	8.92	4.90
	35	4.56	4.48	9.04	5.20

TABLE 3
FREE ENERGY DATA (in kcal mole^{-1}) OF METAL–AMINO ACID COMPLEXES

Amino acid	*T* (°C)	Y^{III}			Ce^{III}
		$-\Delta G_1$	$-\Delta G_2$	$-\Delta G$	$-\Delta G_1$
leucine	25	5.811	5.320	11.131	6.397
	35	6.275	5.921	12.196	6.937
valine	25	6.533	5.824	12.357	6.847
	35	6.471	6.317	12.788	7.360
proline	25	7.365	6.560	13.925	8.198
	35	7.825	7.120	14.945	8.572
hydroxyproline	25	6.165	6.002	12.167	6.683
	35	6.430	6.317	12.747	7.331

TABLE 4
ENTHALPY DATA (in kcal mole^{-1}) OF METAL–AMINO ACID COMPLEXES

Amino acid	Y^{III}			Ce^{III}
	ΔH_1	ΔH_2	ΔH[a]	ΔH_1
leucine	7.986	12.609	20.595	9.666
valine	−8.406	8.826	4.200	8.406
proline	6.304	10.087	16.391	2.942
hydroxyproline	1.681	3.362	5.043	12.609

[a] $\Delta H = \Delta H_1 + \Delta H_2$ calculated from formation constants at 25 and 35°C.

complexes than leucine. Thus lengthening of chain of α-amino acids with increase in molecular weight also decreases the stability. Similar results of a decrease in the stability of α-amino acid complexes with increase in chain length were reported by Malley and Mellor[10].

From Table 4, it is evident that the reactions of cerium and yttrium with all amino acids are endothermic. It is seen from Table 5 that in all systems, entropy

TABLE 5

ENTROPY DATA (in cal degree^{-1} mole^{-1}) ON METAL–AMINO ACID COMPLEXES

Amino acid	T (°C)	Y^{III}			Ce^{III}
		ΔS_1	ΔS_2	ΔS	ΔS_1
leucine	25	46.275	60.134	106.409	53.875
	35	46.279	60.152	106.411	53.880
valine	25	−6.282	49.136	42.854	51.159
	35	−6.279	49.141	42.862	51.163
proline	25	45.846	55.834	101.680	37.360
	35	45.850	55.840	101.690	37.355
hydroxyproline	25	26.315	31.406	57.721	64.705
	35	26.321	31.410	57.731	64.708

changes (ΔS) are always positive. The reaction between an amino acid anion and a cation would result in a decrease of the number of free charged ions in the solution. As a result of this, the entropy term (ΔS) strongly favours complex formation[11]. Thus chelation effect is believed to be essentially an entropy effect. The data obtained on the stabilites of these complexes of tervalent yttrium and cerium with amino acids suggest that many elements, including rare earth elements, enter into the structures of various enzymes, hormones and vitamins, forming physiologically active complexes with proteins.

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