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A Thermodynamic Study of Complexation Reaction of Yttrium(III), Lanthanum(III) and Cerium(III) with Tyrosine

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The thermodynamic stability constants and thermodynamic parameters for complexation reaction of Y^{3+}, La^{3+}, and Ce^{3+} with tyrosine have been determined pH metrically. The study reveals the formation of 1 : 1 complexes for La^{3+} and Ce^{3+} whereas Y^{3+} yields both 1 : 1 and 1 : 2 complexes. The values of enthalpy changes ($\Delta H°$) indicate that unionised hydroxy group also participates in complexation.

The capacity of amino acids to form metal complexes is of theoretical and practical significance[1]. Complexes of lanthanons with amino acids have been extensively studied[2, 3] but little work appears to have been reported for complexes of tyrosine[4–7]. The present paper deals with the study of complexes of Y^{3+}, La^{3+}, and Ce^{3+} with tyrosine in aqueous solution at 0.1, 0.2, or 0.3M ionic strength (KNO_3) and at three temperatures. Most of the amino acids are present as the monoprotonated form HL^- in the pH region 2.7 to 8.5, but a few amino acids occur as H_2L and H_2L^+ form over the whole range. This is true for tyrosine where protons of the phenolic group are not released. In the present investigation, the complexation was observed to take place in the pH region 6.5 to 8.0 and therefore tyrosine has been taken as HL^-.

Experimental

All chemicals used were either BDH or Aldrick AnalaR quality. The ligand solution was prepared in CO_2 free conductivity water immediately before use. Metal nitrate solutions were standardised before use. pH metric titrations were carried out at 25, 35, 45 °C in a thermostat bath against carbonate free 0.1M-KOH solution. A photovolt digicord pH meter having a sensitivity of 0.002 units was used and calibrated with suitable buffers.

Procedure

The mole ratio of metal to ligand was kept 1 : 5 in order to fulfil the maximum coordination number of the metal. The following solutions (total volume 50 ml) were prepared:

A: 5 ml of $1.0 \times 10^{-2} M$-HNO_3
B: 5 ml of $1.0 \times 10^{-2} M$-HNO_3 + 20 ml of $0.625 \times 10^{-2} M$-ligand
C: 5 ml of $1.0 \times 10^{-2} M$-HNO_3 + 20 ml of $0.625 \times 10^{-2} M$-ligand + 2.5 ml of $1.0 \times 10^{-2} M$-metal nitrate.

An ionic strength of 0.1, 0.2 or $0.3 M$ was established by the addition of the calculated amount of KNO_3 ($1.0 M$). The plots of pH versus the volume of the alkali required to obtain the corresponding pH change were plotted. The shapes of the titration curves were as usual.

In order to determine the protonation constant and metal-ligand stability constants, the *Calvin—Bjerrum*[8, 9] pH titration technique as adopted by *Irving* and *Rossotti*[10] was used. In calculation, concentrations were corrected for changes in volume produced by the addition of alkali. The calculated error in stability constants is ± 0.01 $\log K$. The error in ΔG°, ΔH° values lies in the range 0.2 to 0.5 kcals/mole and that for ΔS° is 0.5 cal/degree mole.

Results and Discussion

The proton-ligand formation curve was obtained by plotting the degree of formation ($\bar{n}_H$) of the proton-ligand complex against pH value using the relationship derived by *Irving* and *Rossotti*[10]. Proton-ligand stability constant (amino functional group) has been obtained as *Bjerrum* half integral, pointwise calculation method and graphical methods[9, 11]. Likewise formation constants have been obtained by plotting $\bar{n}$ versus pL. The values of $\bar{n}$, the average number of ligands attached per metal ion are calculated from the equation of *Irving* and *Rossotti*[10] (1).

$$\bar{n} = \frac{(V''' - V'')(N + E^0)}{(V^0 + V')\,\bar{n}_H\,T_M{}^0} \qquad (1)$$

and free ligand exponent pL has been calculated from the equation (2)

$$\mathrm{p}L = \log_{10} \left\{ \frac{\sum_{n=0}^{n=J} \beta_n{}^H \left(\frac{1}{\text{anti}\log \beta} \right)^n}{T_L{}^0 - \bar{n}\,T_m{}^0} \cdot \frac{V' + V'''}{V^0} \right\} \qquad (2)$$

The value of $\bar{n}$ approaches 2 between pH 6.5 to 8.0 for the chelate of tyrosine with Y^{3+} indicating, thereby, the formation of 1 : 1 and 1 : 2 complexes. For La^{3+} and Ce^{3+} complexes the study reveals the formation of 1 : 1 complexes. The values of concentration stability constants

Table 1. *Protonation Constant of the Ligand, Stepwise and Overall Metal-Ligand Stability Constants of the Complexes and Thermodynamic Parameters at Three Temperatures*

Cation	Constant	Temp.			$-\Delta G^\circ$ (kcal/mole)			ΔH° (kcal/mole) at 35 °C	ΔS° (kcal/mole/degree) at 35 °C
		25 °C	35 °C	45 °C	25 °C	35 °C	45 °C		
	$\log K_1^H$*	9.18	9.20	9.23					
Y^{3+}	$\log K_1$	4.43	4.92	5.41	6.0	6.9	7.8		
	$\log K_2$	4.05	4.43	4.81	5.5	6.2	7.0		
	$\log \beta_2$	8.48	9.35	10.22	11.5	13.1	14.8	37.8	165.2
La^{3+}	$\log K_1$	3.82	4.12	4.42	5.2	5.8	6.4	13.0	61.5
Ce^{3+}	$\log K_1$	4.17	4.56	4.95	5.6	6.4	7.2	16.9	88.6

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* Amino functional group.

at various temperatures and at $0.1M$ ionic strength are given in Table 1. The order of stability is $Y^{3+} > Ce^{3+} > La^{3+}$ as expected from their electronic configuration. The data show an increase in log K_1 and log K_2 values with increase in temperature which indicate that higher temperature is favourable for complex formation. The stability decreases with the increase in ionic strength. The values of log step formation constant at various ionic strength extrapolated to zero ionic strength.

The values of stepwise changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) at 35 °C and at $0.1M$ ionic strength are given in Table 1. These have been determined using temperature coefficient and *Gibbs—Helmholtz* equation. The free energies of formation (ΔG°) have more negative value with increase in temperature showing that complex formation is a spontaneous process. The formation of all complexes is an endothermic reaction and it explains the increase in the values of formation constants with rise in temperature. *Letter*, *Bauman* and others[6, 13, 14] have reported that in case of tyrosine, serine and threonine complexes, amino nitrogen and carboxylic oxygen are coordinating and the unionised hydroxy group does not participate. However, *Gergely*, *Mojazes*, and *Bazsa*[15] on the basis of thermodynamic data are of the opinion that larger enthalpy changes associated with formation of serine complexes than those of glycine complexes can only be caused by the increase in the number of bonds. In view of this and a comparison of stability constant data for tyrosine complexes with those of serine we thin k that increased stability of tyrosine complexes and large enthalpy changes may be attributed to back coordinagave log step thermodynamic formation constants[12]. Likewise overall thermodynamic stability constant was obtained (Table 2).

Table 2. *Protonation Constant and Stability Constants of Tyrosine at 35 °C and at Three Ionic Strengths*

Ionic strength	$\log K_n$	H^+	Y^{3+}	La^{3+}	Ce^{3+}
$0.30M$	$\log K_1$	9.15	4.79	3.98	4.43
	$\log K_2$	2.19	4.29		
	$\log \beta_2$		9.08		
$0.20M$	$\log K_1$	9.17	4.85	4.05	4.49
	$\log K_2$	2.21	4.37		
	$\log \beta_2$		9.22		
$0.10M$	$\log K_1$	9.20	4.92	4.13	4.56
	$\log K_2$	2.23	4.43		
	$\log \beta_2$		9.35		
$\to 0$	$\log K_1$	9.24	5.09	4.23	4.65
	$\log K_2$	2.26	4.60		
	$\log \beta_2$		9.69		

tion because of effect of the phenolic hydroxy group[15, 16]. The entropy ($\Delta S°$) values are positive in all cases indicating favourable entropy for formation of complexes.

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