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Note

Stability constants and thermodynamic functions of praseodymium(III), neodymium(III) and samarium(III) with tyrosine

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The capacity of amino acids 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], little work appears to have been reported for complexes of tyrosine[3–7]. The present paper deals with the study of complexes of tyrosine with Pr^{3+}, Nd^{3+} and Sm^{3+} in aqueous solution at 0.1 ionic strength (KNO_3). Most of the amino acids are present as single protonated from HL in the pH region 2.7 to 8.5. A few amino acids occur as H_2L, 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 reaction was observed to take place in the narrow range of 6.5 to 8.0, and therefore tyrosine has been taken as $H\bar{L}$.

EXPERIMENTAL

All chemicals used were either BDH or Aldrich AnalaR quality. The solution of the ligand and metal nitrate were prepared in CO_2-free conductivity water. pH metric titrations were carried out with carbonate-free 0.1 M KOH. The concentration of the ligand was always 2.5×10^{-2} M and that of the metal ion 5×10^{-3} M. An appropriate quantity of potassium nitrate (1 M) solution was added to maintain a constant ionic strength of 0.1 M. Dry nitrogen was bubbled to ensure the absence of oxygen and carbon dioxide. The stability constants of the metals and proton complexes were determined at 25 ± 0.1; 35 ± 0.1 and 45 ± 0.1 °C in a thermostat bath using the Calvin-Bjerrum pH titration technique[8,9]. pH was measured on a Digicord pH meter having a sensitivity of ±0.002 and was calibrated with suitable buffers before use. At the end of each titration, a curve was plotted between the volume of KOH consumed and the corresponding pH. The shapes of the curves were as usual. In our calculations, the concentrations were corrected for the change in volume produced by the addition of alkali during titration.

TABLE 1

PROTONATION CONSTANTS OF THE LIGAND. STEPWISE AND OVERALL METAL-LIGAND STABILITY CONSTANTS OF THE COMPLEXES AND THERMODYNAMIC PARAMETERS AT THREE TEMPERATURES

Metal ion	*Protonation constants/metal-ligand stability constants*	*Temperature (°C)*			*−ΔG (kcal mol⁻¹)*			*ΔH° (kcal mol⁻¹) at 35°C*	*ΔS° (cal mol⁻¹ °C⁻¹) at 35°C*
		25	*35*	*45*	*25°C*	*35°C*	*45°C*		
	$\log {}^{P}K_{1}^{H}$	9.18	9.20	9.23					
Pr^{3+}	$\log K_1$	4.35	4.68	5.01	5.9	6.6	7.3		
	$\log K_2$	3.88	4.12	4.36	5.3	5.8	6.3		
	$\log \beta_2$	8.23	8.80	9.37	11.2	12.4	13.6	24.7	120.4
Nd^{3+}	$\log K_1$	4.54	4.79	5.04	6.2	6.8	7.3		
	$\log K_2$	4.01	4.24	4.48	5.5	6.0	6.5		
	$\log \beta_2$	8.55	9.03	9.52	11.7	12.8	13.8	22.8	115.5
Sm^{3+}	$\log K_1$	4.71	4.91	5.10	6.4	6.9	7.4		
	$\log K_2$	4.13	4.38	4.63	5.6	6.2	6.7		
	$\log \beta_2$	8.84	9.29	9.72	12.0	13.1	14.1	19.3	105.2

RESULTS AND DISCUSSION

$\bar{n}_H$, $\bar{n}$, pL were calculated by employing the relationships derived by Calvin and Wilson[8]. The proton-ligand formation curve was obtained by plotting the degree of formation ($\bar{n}_H$) of the proton complex against the pH value. The proton-ligand stability constant $\log K_1^H$ (amino functional group) of the ligand has been obtained by the Bjerrum half integral method[9], also by pointwise calculation and graphical methods[10]. The complex-ligand formation curve was then obtained by plotting $\bar{n}$ versus pL. Metal-ligand stability constants were determined by the Bjerrum half integral method, pointwise calculation and graphical methods using the following equation :

$$\log K_1 = \mathrm{pL} - \log \frac{1-\bar{n}}{\bar{n}}$$

$$\log K_2 = \mathrm{pL} - \log \frac{2-\bar{n}}{\bar{n}-1}$$

The values of overall changes in free energy ($\Delta G°$), enthalpy $\Delta H°$ and entropy $\Delta S°$ have been determined by using the well-known temperature coefficient and Gibbs-Helmholtz equation[11]. The mean values of the protonation constant, stability constants and thermodynamic parameters are summarized in Table 1. The calculated error in the stability constants is $\pm 0.01 \log K$. The error in $\Delta G°$ and $\Delta H°$ values calculated from stability constants lie in the range 0.2 to 0.5 kcal mol^{-1} and that for $\Delta S°$ is 0.5 cal °C^{-1} mol^{-1}.

The values of $\bar{n}$ approach 2 for Pr^{3+}, Nd^{3+}, Sm^{3+} chelates with tyrosine indicating the formation of 1:1 and 1:2 complexes. The order of the overall stability of these complexes is $Sm^{3+} > Nd^{3+} > Pr^{3+}$ at 25, 35 and 45°C as expected from their electronic configuration. The data show an increase in value of $\log K_1^H$, $\log K_1$ and $\log K_2$ with increase in temperature. This shows that a higher temperature is favourable for the formation of complexes because of an increased number of collisions with increase in kinetic energy of the molecules and their stabilities are enhanced. Comparison of metal-ligand stability constant values of tyrosine with those of serine leads to the conclusion that the unionized hydroxy group is not participating in complex formation[6,12]. The free energies of formation ($\Delta G°$) have a 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. The entropy ($\Delta S°$) values are positive in all cases indicating a favourable entropy for the formation of complexes.

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