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Complex Formation Constants and Thermodynamic Parameters for La(III) and Y(III) *L*-Serine Complexes

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Summary. The stoichiometric stability constants for La(III) and Y(III) *L*-serine complexes were determined by potentiometric methods at different ionic strengths adjusted with $NaClO_4$ and at different temperatures. The overall changes in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) during the protonation of *L*-serine and that accompanying the complex formation with the metal ions have been evaluated.

Keywords. L-serine; Lanthanum(III) complexes, Yttrium(III) complexes; Thermodynamic parameters.

Komplexbildungskonstanten und thermodynamische Parameter für La(III)- und Y(III)-*L*-Serin-Komplexe

Zusammenfassung. Die stöchiometrischen Komplexbildungskonstanten für La(III)- und Y(III)-*L*-Serin-Komplexe wurden mittels potentiometrischer Methoden bei verschiedenen Ionenstärken (mit $NaClO_4$ adjustiert) und bei verschiedenen Temperaturen bestimmt. Die Änderungen in der freien Energie (ΔG°), Enthalpie (ΔH°) und Entropie (ΔS°) während der Protonierung und der Komplexbildung mit den Metallionen wurden ermittelt.

Introduction

Extensive work has been reported on amino acid complexes with various metal ions [1 – 3]. Interest in the chemistry of lanthanide-amino acid complexes has been generated in view of their application in biological and pharmaceutical fields [4], besides the ability of using the lanthanide ions as spectroscopic probes of calcium ion binding sites in proteins [5, 6]. Studies of *Ln*(III)-amino acid complexes have received considerable attention to determine their stability constants [7], to ascertain the nature of bonding and to elucidate the structure of these complexes [8]. In continuation to our earlier studies [9], the present work deals with the study of complex formation of *L*-serine with La(III) and Y(III) ions by potentiometric methods. For better understanding of the factors which cause complex formation, it is desirable to calculate the thermodynamic parameters ΔH° and ΔS° and their relative contribution in the free energy change (ΔG°). The most probable reacting species as well as the mode of bonding, will be discussed.

Experimental

L-serine $[^{+}NH_3-CH(CH_2OH)-COO^{-}]$ was obtained as zwitterion from Fluka. Standard *L*-serine solutions (0.05 *M*) and sodium serinate (0.5 *M*) were freshly prepared to avoid photodecomposition. The oxides La_2O_3 (BDH) and Y_2O_3 (Fluka AG, Buchs SG) were dissolved in the minimum amount of $HClO_4$ and the metal contents were determined by complexometric titrations [10]. Standard carbonate-free sodium hydroxide (0.5 *M*) was used for potentiometric titrations. Sodium perchlorate (1 *M*) was used to adjust the ionic strength (μ) at 0.5, 0.1 and 0.15 mol dm^{-3}.

The experimental procedure involved a series of *pH*-titrations of *L*-serine with standard alkali in the absence and in the presence of metal ions at constant ionic strength and temperature using a digital *pH*-meter (PT-I-15). The details of the procedure have been described in the previous paper [9].

Results and Discussion

For the evaluation of the stability constants of La(III) and Y(III) *L*-serine complexes the procedures suggested by Bjerrum [11] and Rossotti [12] were used. Therefore the determination of the ionization equilibria for *L*-serine under the same conditions of ionic strength and temperature, was necessary as well.

For *L*-serine (H_2A), existing as H_3A^+ in the presence of $HClO_4$, the deprotonation constants K_1, K_2, and K_3 were determined by applying mass balance and charge balance equations during the titration of a mixture of 5 mmol *L*-serine and 1 mmol $HClO_4$ (at a given μ and temperature) against standard alkali. Calculations at $pH < 7$, where the species present at equilibrium are H_3A^+ and H_2A, allow the determination of K_1 using Eq. (1). At $8 < pH < 11.5$, where the species present at equilibrium are H_2A, HA^-, and A^{2-}, the deprotonation equilibria K_2 and K_3 could be determined applying Eq. (2),

$$(1+F)/F = -K_1/[H^+], \tag{1}$$

$$F[H^+]/(1-F) = K_2 + K_2K_3\{(2-F)/(1-F)[H^+]\}, \tag{2}$$

where the function

$$F = \frac{[Na^+]+[H^+]-[ClO_4^-]-[OH^-]}{C_L}, \tag{3}$$

C_L is total *L*-serine concentration, $[Na^+]$ is the concentration of NaOH added and $[ClO_4^-]$ is the concentration of $HClO_4$; the concentrations $[H^+]$ and $[OH^-]$ were obtained from the *pH* readings ($-\log a_H^+$) using an activity coefficient (f_H^+) calculated at a given ionic strength [13].

The deprotonation equilibria K_1, K_2, and K_3 for *L*-serine were calculated by applying a linear least square fit of data into Eqs. (1) and (2) at ionic strengths 0.05, 0.1, and 0.15 mol dm^{-3} and at temperatures 20, 27, and 35°C. The values obtained were found to be virtually independent on the ionic strength and hence an average value was taken to be the thermodynamic equilibrium constant (K^T) at each temperature. The thermodynamic parameters ΔH° and ΔS° were evaluated by appling the linear least square method into Van't Hoff's relation given by

$$\ln K^T = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}. \tag{4}$$

Data obtained together with ΔG° ($-RT\ln K^T$) are collected in Table 1.

Table 1. Thermodynamic protonation constants of *L*-serine pK^T at different temperature and their thermodynamic parameters

pK^T	Temperature/°C			ΔS° cal deg^{-1} mol^{-1}	ΔH° kcal mol^{-1}	ΔG° (298°K) kcal mol^{-1}
	20	27	35			
pK_1	2.74	2.38	2.54	–	–	3.27[a]
pK_2	9.30	9.03	8.85	-0.30 ± 0.02	12.37 ± 1.0	12.46 ± 1.0
pK_3	11.93	11.84	11.94	–	–	16.26[a]

[a] ΔG° calculated at 300°K

The results revealed that only thermodynamic parameters ΔH° and ΔS° are calculated for pK_2 (deprotonation of the amine group) since pK_1 and pK_3 are not linearly dependent on temperature. On examining the pK_1 data which correspond to deprotonation equilibria of the $-$COOH group shows that K_1 passes through a maximum with increase of temperature. This behaviour might be ascribed to the fact that ΔH° and ΔS° are functions of temperature as given by Eqs. (5) and (6),

$$\left[\frac{\partial(\Delta H^\circ)}{\partial T}\right]_p = \Delta C_p^\circ \tag{5}$$

and

$$\left[\frac{\partial(\Delta S^\circ)}{\partial T}\right]_p = \Delta C_p^\circ / T, \tag{6}$$

where ΔC_p° is the change in standard heat capacity for the reaction at constant pressure. Similar maxima have been observed for a number of carboxylic acids which is ascribed [14] to two different types of forces between the particles in solution. One is due to covalent bonding and is temperature independent, the other one is ascribed to electrostatic interactions and is temperature dependent. The values of pK_3 (deprotonation of the hydroxyl group) occurs at $pH \simeq 12$ and showed within experimental error no temperature dependence.

The stoichiometric stepwise stability constants based on all species present in solution were determined from the formation curves obtained by plotting $\bar{n}$ (complex formation function) versus pL (free ligand concentration).

This formation curves revealed that at $pH < 6$ slight complex formation was observed as indicated by very low $\bar{n}$ values ($\bar{n} \leqslant 0.04$). At higher pH range (6–8) complex formation was quite evident; $\bar{n}$ increases but does not exceed 0.9 which indicates that only 1 : 1 mononuclear complexes are formed. Above this pH range an insoluble precipitates were observed due to hydrolysis and/or polymerisation of the metal ions [15]; the calculation of $\bar{n}$ was stopped at that stage.

For *L*-serine an equilibrium mixture of H_3A^+, H_2A, HA^-, and A^{2-} would exist. Each of the above species could act as the ligating species. But since complex formation takes place in slightly alkaline medium and because only one equivalent of base per metal ion was consumed during complexation one can conclude that the possible reacting species are limited to either H_2A or HA^- and the interaction of *L*-serine with La(III) or Y(III) would proceed most probably via reactions (7) or (8) with stability constants $\beta_1^{[H_2A]}$ and $\beta_1^{[HA^-]}$, respectively,

$$M^{3+} + H_2A \overset{\beta_1^{[H_2A]}}{\rightleftharpoons} [M(HA)]^{2+} + H^+, \tag{7}$$

$$M^{3+} + HA^- \overset{\beta_1^{[HA^-]}}{\rightleftharpoons} [M(HA)]^{2+}. \tag{8}$$

These constants are related to each other via K_2 of *L*-serine ($pK_2 = 9.3 - 8.85$).

The stoichiometric stability constant ($\beta_1^{[HA^-]}$) for La(III) and Y(III) *L*-serine complexes were evaluated from the formation curves ($\bar{n}$ versus pL) by the half integral method [12] and other computional methods [16]. At slightly alkaline medium the free ligand concentration (pL) in terms of the reacting species $[HA^-]$ could be calculated using relation (9),

$$pL_{[HA^-]} = \log\{(1 + K_3/[H^+] + [H^+]/K_2)/C_L - \bar{n}C_M\}, \tag{9}$$

where C_L and C_M are the total *L*-serine and total metal ion concentration (La^{3+} or Y^{3+}), respectively and K_2 and K_3 are the second and the third dissociation constants of *L*-serine.

The thermodynamic stability constants ${}^T\beta_1^{[HA^-]}$ for La(III) and Y(III) complexes at each temperature studied (20, 27 and 35°C) were obtained from linear plots of $\log \beta_1^{[HA^-]}$ versus μ ($\mu = 0.05$, 0.1 and 0.15 mol dm^{-3} using $NaClO_4$) and extrapolating to $\mu = 0$. The data obtained together with the thermodynamic parameters (ΔH°, ΔG°, and ΔS°) are summarized in Table 2.

From the results obtained it has been concluded that *L*-serine forms 1 : 1 complexes with La(III) and Y(III) ions at the *pH* range 6 – 8. The small magnitude of the stability constant ${}^T\beta_1^{[HA^-]}$ of these complexes revealed that *L*-serine is a weak complexing agent at the *pH* range studied. This behaviour is quite general for interactions of amino acids with lanthanides in neutral or weakly alkaline media [17]. The negative value of ΔG° indicate that these complexes are formed spontaneously which is attributed to the high positive ΔS° term. The positive values of ΔH° show that the reactions are endothermic, the large positive ΔS° revealed that the complex formations are entropy favoured.

Also, it is obvious that in the *pH* range studied *L*-serine could act as a bidentate ligand coordinating via one of the carboxylic oxygens ($pK_1 = 2.38 - 2.74$) and the

Table 2. Thermodynamic stability constants ${}^T\beta_1^{[HA^-]}$ and thermodynamic parameters for La(III) and Y(III) L-serine complexes

Metal ion	log ${}^T\beta_1^{[HA^-]}$ ($\mu = 0$) at different temperature/°C			ΔS° cal deg^{-1} mol^{-1}	ΔH° kcal mol^{-1}	ΔG° (298°K) kcal mol^{-1}
	20	27	35			
La(III)	3.18	3.24	3.34	30.20 ± 0.02	4.62 ± 0.9	−4.38 ± 0.9
Y(III)	3.50	3.67	3.76	35.67 ± 0.04	5.72 ± 0.9	−4.91 ± 1.0

amine nitrogen ($pK_2 = 8.85 - 9.30$). The hydroxyl group ($pK_3 \simeq 11.9$) though still protonated, may probably be involved in the co-ordination process since its deprotonation was not detected by potentiometric measurements during or prior to complex formation (no more than one equivalent of base per metal ion was consumed during complexation). This latter assumption was in agreement with the NMR shifts of Nd-*L*-serine complexes [18], which indicates that at *pH* 6.5 *L*-serine probably binds Nd(III) in a trindentate manner. The data obtained also reflect an increase in the stability constant ${}^{T}\beta_1^{[HA^-]}$ when going from La^{3+} to Y^{3+}; this should be expected due to the decreasing ionic radii ($La^{3+} = 1.06$ Å and $Y^{3+} = 0.88$ Å).

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