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A Thermodynamic Study of La(III)*L*-Alanine Complexes

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Summary. The protonation constants of *L*-alanine and the complex formation constants of its La(III) complexes were determined by potentiometric studies at ionic strengths 0.06, 0.1, and 0.15 mol dm^{-3} ($NaClO_4$) and at different temperatures 20, 27, and 35 °C. The data together with the derived thermodynamic parameters ΔH°, ΔS°, and ΔG° are reported and discussed.

Keywords. Lanthanum complexes; L-Alanine; Potentiometry; Thermodynamic parameters.

Eine thermodynamische Untersuchung der La(III)-*L*-Alanin-Komplexe

Zusammenfassung. Die Protonierungskonstanten von *L*-Alanin und die Komplexbildungskonstanten der La(III)-Komplexe wurden potentiometrisch bei den Ionenstärken 0.06, 0.1 und 0.15 mol dm^{-3} ($NaClO_4$) bei den Temperaturen 20, 27 und 35 °C bestimmt. Diese Daten und die abgeleiteten thermodynamischen Parameter ΔH°, ΔS° und ΔG° werden diskutiert.

Introduction

Aminoacids are of great biological importance as many of them are essential for human life. The importance of such acids stems from their presence as building blocks in protein molecules which are in turn building blocks of enzymes [1]. The rare earth elements seem to play no significant part in biological systems. In fact, lanthanide ions possess unique chemical properties and are often used as excellent probes [2] for the interaction of Ca^{2+} ion with biological systems. Since Ln^{3+} ions can substitute the Ca^{2+} ion, the interaction of amino acids with lanthanide ions seemed reasonable. Extensive work has been reported [3–6] on such interactions to determine the stability constants of the formed complexes and to ascertain the mode of bonding. Recently spectroscopic and crystallographic [7] studies are used to elucidate the structure of these complexes.

The present work was intended to study the interaction between La(III) and *L*-alanine by potentiometric methods. The thermodynamic stability constants and the thermodynamic parameters are evaluated and discussed. If possible, the mode of bonding will be ascertained together with the nature of the ligating species.

Experimental

L-Alanine was obtained as free base (zwitterion) from Fluka Garantie, La_2O_3 (B.D.H. Analar Grade) was dissolved in a calculated amount of $HCLO_4$ and the metal content was determined by complexometric titrations [8]. Standard *L*-alanine (0.05 *M*) and 0.4 *M* sodium alaninate were freshly prepared. Standard carbonate-free sodium hydroxide was pepared and used for potentiometric titrations. All other chemical reagents used were of Analar Grade.

A digital *pH*-meter (PT-1-15) was employed and thermostated at the desired temperature.

The experimental procedure involved a series of *pH*-metric titrations as adopted by Bjerrum's [9] and Rossotti's [10] techniques where the *pH* were recorded as a function of

(a) Perchloric acid or sodium hydroxide added to 100 ml solution containing 5 mmol *L*-alanine,
(b) sodium alaninate (0.4 *M*) added to 200 ml solution containing 1 mmol $HClO_4$ + 1 mmol $La(ClO)_3$,
(c) sodium hydroxide (0.5 *M*) added to 200 ml solution containing either (i) 1 mmol $HClO_4$, (ii) 1 mmol $HClO_4$ + 5 mmol *L*-alanine, and (iii) 1 mmol $HClO_4$ + 5 mmol *L*-alanine + 1 mmol $La(ClO_4)_3$.

Each of the above solutions was adjusted at the desired $\mu = 0.06$, 0.1, and 0.15 using $NaClO_4$ and thermostated at 20, 27, and 35 °C with an accuracy of ±0.02 °C.

Results and Discussion

For the determination of the "stoichiometric" protonation constands of *L*-alanine (H*A*) present always as zwitterion $[H_3N^+ - CH(CH_3) - COO^-]$ the following equilibria were considered:

$$H_2A \overset{K_1}{\rightleftharpoons} HA + H^+ , \tag{1}$$

$$HA \overset{K_2}{\rightleftharpoons} A^- + H^+ . \tag{2}$$

Potentiometric titrations of *L*-alanine (adjusted at a given μ and temperature) with either $HClO_4$ or NaOH allow determination of pK_1 and pK_2 using the following equations, respectively, where

$$pK_1 = -\log[H^+] + \log\frac{[ClO_4^-] + [OH^-] - [H^+]}{[A_{tot}] - [ClO_4^-] - [OH^-] + [H^+]} \tag{3}$$

and

$$pK_2 = -\log[H^+] + \log\frac{[A_{tot}] - [H^+] - [Na^+] + [OH^-]}{[H^+] + [Na^+] - [OH^-]}, \tag{4}$$

given that $[A_{tot}]$ is the total *L*-alanine concentration, $[ClO_4^-]$ is the concentration of $HClO_4$ added, and $[Na^+]$ is the concentration of NaOH added. Each one of the concentrations was corrected for volume changes during the titrations.

The hydrogen and hydroxyl ion concentrations $[H^+]$ and $[OH^-]$ in Eqs. (3) and (4) were obtained from the *pH* readings ($-\log a_{H^+}$) applying Davies equation [11] at a given ionic strength assuming that

$$\log[H^+] = -pH - \log\gamma_\pm \tag{5}$$

and

$$\log[OH^-] = pH - \log\gamma_\pm - pK_w, \tag{6}$$

where $\gamma_\pm$ is the mean activity coefficient.

Final values of pK_1 and pK_2 showed little ionic strength dependences ($0.06 < \mu < 0.15$) and an average value for each was taken to be the "thermodynamic" equilibrium constant (K^T) at a given temperature. The thermodynamic parameters ΔH° and ΔS° were obtained by linear least square fit of ln K^T versus $1/T$ leading to an intercept $\Delta S^\circ/R$ and a slope $-\Delta H^\circ/R$. The standard free energy (ΔG°) at 298 °K was then calculated using the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ . \qquad (7)$$

The results obtained are summarized in Table 1.

The stoichiometric stability constants of La(III)*L*-alanine complexes were computed from ($\bar{n}$) complex formation function and [L] free ligand concentration by methods following Bjerrum [9] and Rossotti [10]. Analyses of $\bar{n}$-ligand anion added (Bjerrum's method) or $\bar{n}$-base added (Rossotti's method) revealed that at low *pH* values (3–6.5) no complexation or very weak interactions are taking place. This was evidenced by very low $\bar{n}$ calculated ($\bar{n} < 0.05$). In the range (6.5–8) only mononuclear complexes were observed ($\bar{n} < 0.9$). Above *pH* 8 base hydrolysis commences and insoluble precipitates are formed. The *pH* titration was stopped at this stage. The $\bar{n}$ data upon which the stability constants evaluation was based were, however, limited to a maximum of *pH* 7.8, to avoid erroneous calculations due to hydrolysis and/or polymerization.

In the absence of a priori knowledge of the ligating species, the stability constants were calculated based on all possible reacting species. In case of *L*-alanine an equilibrium mixture H_2A^+, HA, and A^- exists. Each of these species could act as the ligating species. But since complex formation was observed at neutral or slightly basic *pH*'s with release of one equivalent of hydrogen ions (one equivalent of base was consumed during complex formation), then the reacting species are limited to either HA or A^-. The most probable reactions could be given as

$$\mathrm{La}^{3+} + \mathrm{H}A \overset{\beta_{1[\mathrm{H}A]}}{\rightleftharpoons} \mathrm{La}A^{2+} + \mathrm{H}^+ , \qquad (8)$$

$$\mathrm{La}^{3+} + A^- \overset{\beta_{1[A^-]}}{\rightleftharpoons} \mathrm{La}A^{2+} , \qquad (9)$$

where $\beta_{1\,[\mathrm{H}A]}$ and $\beta_{1\,[A^-]}$ are related to each other via K_2 of *L*-alanine as given by

$$\beta_{1\,[\mathrm{H}A]} = \beta_{1\,[A^-]} \cdot K_2 . \qquad (10)$$

These complex formation constants $\beta_{1\,[\mathrm{H}A]}$ and $\beta_{1\,[A^-]}$ were calculated from the formation curves ($\bar{n}$ versus pL) at $\bar{n} = 0.5$ and were refined by other computational methods [10]. The free ligand concentration of *L*-alanine in terms of the reacting species HA or A^- could be calculated using the following relations,

$$[L]_{\mathrm{H}A} = \frac{C_L - \bar{n}\, C_M}{1 + [\mathrm{H}^+]/K_1 + K_2/[\mathrm{H}^+]} \qquad (11)$$

and

$$[L]_{[A^-]} = \frac{C_L - \bar{n}\, C_M}{1 + \mathrm{H}^+/K_2 + [\mathrm{H}^+]^2/K_1 K_2} , \qquad (12)$$

where C_L and C_M are the total *L*-alanine and metal concentrations, and K_1 and K_2 are the first and the second ionization constants of *L*-alanine.

These constants were calculated at different ionic strengths ($0.06 < \mu < 0.15$) and at different temperatures. The results revealed that no significant ionic strength

Table 1. Thermodynamic protonation constants of *L*-alanine, thermodynamic stability constants of La(III)-*L*-alanine complexes at different temperatures and their thermodynamic parameters

Thermodynamic constants	Temperature °C 20	27	35	ΔS° cal deg^{-1} mol^{-1}	ΔH° kcal mol^{-1}	ΔG° (298 °K) kcal mol^{-1}
L-Alanine						
PK_1^T	2.18	2.02	1.93	13.94 ± 0.01	6.86 ± 0.7	2.84 ± 0.7
PK_2^T	9.69	9.54	9.43	−19.92 ± 0.01	7.15 ± 0.5	13.09 ± 0.5
La(III) complex						
$\log \beta_1^T(\mathrm{H}A)$	−6.49	−6.24	−5.95	21.09 ± 0.01	14.89 ± 0.2	8.61 ± 0.2
$\log \beta_1^T(A^-)$	3.20	3.30	3.48	41.02 ± 0.01	7.75 ± 0.6	−4.47 ± 0.6

dependences were observed and average values were taken to be the thermodynamic constants given as $\beta_{1[\mathrm{H}A]}^T$ and $\beta_{1[A^-]}^T$. The thermodynamic parameters ΔH°, ΔS° and ΔG° (298 °K) were also calculated. The data obtained are reported in Table 1.

The data obtained revealed that at the *pH* range of this study only 1 : 1 complexes formed, whereby at low *pH* range 3–6 *L*-alanine coordinates weakly to La(III) via the deprotonated carboxyl group (pK_1 2.18–1.93). In the *pH* range 6–8 binding of the orther deprotonated group (amine nitrogen $pK_2 \simeq 9.69$–9.43) with La(III) is possible. The weak interaction between La(III) and *L*-alanine is evidenced by the small magnitude of stability constants and the endothermic nature of ΔH°. The negative value of ΔG° and hence the spontaneity (though small) of reaction (9) is attributed to the high positive ΔS° term – the reaction is entropy favoured. All the data reported [13] are consistent with quite weak bonding between the lanthanides and amino-acids as evidenced from the rather low formation constants values.

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