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THERMODYNAMIC PARAMETERS FOR THE FORMATION OF CALCIUM α-ALANINATE COMPLEXES IN AQUEOUS SOLUTION

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ABSTRACT

The formation constants of $[Ca(ala)]^+$ and $[Ca(ala)H]^{2+}$ (ala = α-alaninate) complexes have been determined potentiometrically at several temperatures ($10 \leq T \leq 50\,^\circ C$) and ionic strengths ($0.04 \leq I \leq 1$ mol l^{-1}). Since tetraethylammonium (Et_4N^+) and sodium salts have been used as reference backgrounds, the interactions of these salts with α-alaninate have been also studied. The following very unstable species have been found: $[Na(ala)]^0$, $[Na(ala)H]^+$, $[Et_4N(ala)]^0$, $[(ala)HCl]^-$ and $[(ala)H_2Cl]^0$. ΔH° values for the formation of all these species were obtained from the dependence on temperature of the formation constants.

INTRODUCTION

The formation of calcium complexes with aminoacids has been little studied owing to their instability [1]. In addition, the presence of two different groups, one of which (carboxylate) can form unstable species with alkali metals [2–4] and the other (amino group) that can form unstable species with tetraalkylammonium cations [5,6] and, when protonated, can form ion pairs with the anion of the background electrolyte [5,6], makes the speciation of the system aminoacid–calcium–background quite complicated. On the other hand, aminoacids and calcium are present in several natural fluids and the formation of calcium–aminoacid complexes must be known in order to have a correct speciation of these fluids. In the last decade the authors and some colleagues dedicated much effort to studying weak interactions (refs. 5 and 6 and references therein) and to building up models for natural fluids in which weak interactions occur. Therefore, we decided to begin a new series of investigations on the formation of aminoacid complexes with alkali and alkaline earth metal cations. Here, we report a

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potentiometric study of the system α-alanine–NaCl–$CaCl_2$–Et_4NI at different temperatures and ionic strengths.

EXPERIMENTAL

Materials

α-Alanine (Fluka purum, p.a.) was used without purification; its purity, checked by alkalimetric titration, was always $\geq 99.7\%$. Hydrochloric acid and potassium hydroxide standard solutions were prepared by diluting concentrated ampoules (C. Erba or Merck) and standardized against sodium carbonate and potassium biphthalate, respectively. Tetraethylammonium bromide or iodide (Et_4NBr, Et_4NI, Fluka or C. Erba) were recrystallized twice from methanol [7]. Sodium chloride solution was prepared from Fluka purum. p.a. product, dried in a stove at 110 °C; calcium chloride solution was prepared from Fluka purum p.a. product and standardized against EDTA [8]. Twice-distilled water and grade A glassware were employed.

Apparatus

Hydrogen-ion concentrations were measured with a Metrohm E605 potentiometer, equipped with a Metrohm glass electrode and an Ingold calomel electrode. The titrant was delivered by an Amel dispenser or a Metrohm motorized burette, both having a minimum reading of 0.001 ml. The calibration of electrode couple, in $-\log C_H$ units (C_H = free proton concentration), was achieved by titrating hydrochloric acid (10–20 mmol l^{-1}) with standard carbonate-free potassium hydroxide under the same conditions as the solution considered (i.e. the same temperature, ionic strength and background salt). The reliability of the calibration in the alkaline range was checked by calculating pK_w values. The measurement cell was thermostated at $T \pm 0.2$ °C. Magnetic stirring was employed. A steam of purified nitrogen was bubbled through the solution in order to exclude CO_2 and O_2.

Procedure

The titrations were carried out on 25 ml of solution containing 6 mmol l^{-1} of ligand, variable amounts of Et_4NBr (or Et_4NI), NaCl and $CaCl_2$ as background salts, and 16 mmol l^{-1} of HCl. Six duplicate titrations were performed for each background (C_{M^+} = 24, 134, 234, 474, 624 and 984 mmol l^{-1} ($M^+ = Na^+$, Et_4N^+); $C_{Ca^{2+}}$ = 8, 48, 78, 158, 208 and 328 mmol l^{-1}). HCl was added in order to complete protonation of α-alanine, and to calculate directly the internal E° (E°_{int}); by separate calibration we calculated E°_{ext}. If $|E^\circ_{int} - E^\circ_{ext}| > 1.5$ mV the titration was rejected.

Calculations

Potentiometric data were first analyzed by the least squares computer program ESAB2M [9], which refines the values of conditional protonation constants, along with E°, log K_w, and analytical concentrations (when necessary). Formation constants of weak complexes were refined by the least squares computer program ES2WC [10]. Concentrations and thermodynamic quantities are always expressed on the molar scale. The dependence on ionic strength of formation constants was taken into account by using the semiempirical equation

$$\log K = \log {}^{\mathrm{T}}K - z^*\sqrt{I}/(2+3\sqrt{I}) + CI + DI^{3/2}$$

$$= \log {}^{\mathrm{T}}K - z^*G(I) + L(I) \qquad (1)$$

with

$$C = c_0 p^* + c_1 z^*; \quad D = dz^* \qquad (2)$$

where log ${}^{\mathrm{T}}K$ is the formation constant at infinite dilution, $z^* = \Sigma(z^2_{\mathrm{reactants}} - z^2_{\mathrm{products}})$; $p^* = \Sigma(p_{\mathrm{reactants}} - p_{\mathrm{products}})$; and c_0, c_1 and d are empirical parameters (z, charges; p, stoichiometric coefficients). According to our previous results [3,4,11], at 25 °C

$$c_0 = -d = 0.1; \quad c_1 = 0.23 \qquad (3)$$

with [12]

$$\partial c_0/\partial T = -0.0012; \quad \partial c_1/\partial T = -0.0011; \quad \partial d/\partial T = 0.0012 \qquad (4)$$

when allowing for all the interactions occurring in the system under investigation.

RESULTS AND DISCUSSION

Potentiometric data were first analyzed without taking into account any interaction with the background salt. Therefore we calculated conditional protonation constants, reported in Table 1. Log ${}^{\mathrm{T}}K^{\mathrm{H}}$ values extrapolated to zero ionic strength, together with ΔH° values deduced from the dependence on temperature, are reported in Table 2. These values are in agreement with literature data [1]. In Table 3 we report some conditional $\Delta H^{\circ\prime}$ values. C and D values of eqn. (1) were calculated for log $K_1^{\mathrm{H}\prime}$ and log $K_2^{\mathrm{H}\prime}$ (primes indicate conditional protonation constants) as reported in Table 4. As one can see, these values are quite different for the different backgrounds and are also different from the predicted values (log K_1^{H}: $C = 0.56$; $D = -0.2$; log K_2^{H}: $C = 0.1$, at 25 °C, from eqns. (2) and (3)).

The differences between conditional protonation constants obtained in different backgrounds were explained by the following speciation model

$(X^- = Cl^-, Br^- \text{ or } I^-)$

$\text{ala}^- + H^+ = [(\text{ala})H]^0 \qquad K_1^H$

$[(\text{ala})H]^0 + H^+ = [(\text{ala})H_2]^+ \qquad K_2^H$

$\text{ala}^- + Na^+ = [Na(\text{ala})]^0 \qquad K_1^{Na}$

$[(\text{ala})H]^0 + Na^+ = [Na(\text{ala})H]^+ \qquad K_2^{Na}$

$\text{ala}^- + Ca^{2+} = [Ca(\text{ala})]^+ \qquad K_1^{Ca}$

$[(\text{ala})H]^0 + Ca^{2+} = [Ca(\text{ala})H]^{2+} \qquad K_2^{Ca}$

$[(\text{ala})H]^0 + X^- = [(\text{ala})HX]^- \qquad K_1^X$

$[(\text{ala})H_2]^+ + X^- = [(\text{ala})H_2X]^0 \qquad K_2^X$

$\text{ala}^- + Et_4N^+ = [(\text{ala})Et_4N]^0 \qquad K_1^{Et_4N}$

TABLE 1

Conditional protonation constants of α-alanine in different backgrounds [a]

T (°C)	I (mol l^{-1})	$Et_4N(Br,I)$		NaCl		$CaCl_2$	
		log $K^{H'}$	log $K_2^{H'}$	log $K_1^{H'}$	log $K_2^{H'}$	log $K_1^{H'}$	log $K_2^{H'}$
10	0.04	10.14	2.37	10.11	2.35	10.09	2.38
	0.16	10.10	2.41	10.07	2.37	10.00	2.38
	0.25	10.09	2.44	10.07	2.39	9.97	2.38
	0.49	10.12	2.52	10.10	2.43	9.92	2.39
	0.64	10.14	2.56	10.13	2.45	9.91	2.39
	1.00	10.19	2.68	10.20	2.51	9.88	2.39
25	0.04	9.73	2.39	9.72	2.35	9.70	2.34
	0.16	9.70	2.41	9.68	2.37	9.59	2.35
	0.25	9.70	2.43	9.68	2.38	9.55	2.35
	0.49	9.72	2.48	9.71	2.41	9.50	2.35
	0.64	9.73	2.51	9.74	2.42	9.48	2.36
	1.00	9.74	2.58	9.80	2.47	9.46	2.36
40	0.04	9.35	2.35	9.35	2.33	9.33	2.33
	0.16	9.32	2.38	9.28	2.35	9.20	2.33
	0.25	9.32	2.41	9.26	2.36	9.15	2.33
	0.49	9.35	2.48	9.28	2.39	9.07	2.34
	0.64	9.36	2.52	9.30	2.41	9.04	2.34
	1.00	9.38	2.62	9.39	2.46	9.01	2.35
50	0.04	9.14	2.36	9.10	2.36	9.08	2.33
	0.16	9.09	2.38	9.00	2.37	8.95	2.33
	0.25	9.08	2.41	8.97	2.37	8.90	2.33
	0.49	9.09	2.46	8.97	2.38	8.82	2.33
	0.64	9.09	2.49	8.99	2.39	8.79	2.32
	1.00	9.10	2.57	9.12	2.40	8.77	2.32

[a] $3\sigma(\log K_1^{H'}) = 0.01-0.03$; $3\sigma(\log K_2^{H'}) = 0.02-0.05$.

TABLE 2

Thermodynamic parameters for the protonation of α-alanine

T (°C)	$\log {}^{T}K_1^{H}$	$\log {}^{T}K_2^{H}$	ΔH_1°	ΔH_2°
10	10.245 [a]	2.345 [a]		
25	9.856	2.338		
	(9.867) [b]	(2.348) [b]		
40	9.492	2.342		
50	9.263	2.349		
25			-10.00 [c] ± 0.15	-0.05 [c] ± 0.15
			(-10.8) [b,c]	(-0.7) [b,c]
			-41.9 [d] ± 0.6	-0.2 [d] ± 0.6
			(-45.2) [b,d]	(-2.9) [b,d]

[a] $3\sigma(\log {}^{T}K_1^{H}) = 0.006-0.015$; $3\sigma(\log {}^{T}K_2^{H}) = 0.008-0.02$.

[b] Literature values [1].

[c] ΔH° values in kcal mol^{-1}.

[d] ΔH° values in kJ mol^{-1}.

Calculations performed with ES2WC gave the results reported in Table 5. All the values reported in this table are in fairly good accordance with those reported previously for similar interactions (note that we considered K_1^{X} and K_2^{X} independent of X^-: this assumption was justified by calculations). For example, $\log K_2^{Na} = -0.25$ ($I = 0$, $T = 25$ °C) is comparable with the formation constant of the complex [Na(acetate)]^0, $\log K^{Na} = -0.11$ [13]; $\log K_1^{X} = -0.1$ ($I = 0$, $T = 25$ °C) is comparable with the formation constant of [(piridine)HX]^0, $\log K^{X} = -0.15$ [5]. The formation constants of calcium complexes, K_1^{Ca} and K_2^{Ca}, are in good agreement with those of glycine [4]. As a consequence of the complexity of the system under study,

TABLE 3

Conditional protonation $\Delta H^{\circ\prime}$ values at $T = 30$ °C [a]

Salt	I (mol l^{-1})	$-\Delta H_1^{\circ\prime}$	$-\Delta H_2^{\circ\prime}$	Mean values		
				I	$-\Delta H_1^{\circ\prime}$	$-\Delta H_2^{\circ\prime}$
Et_4NI	0.15	44.6	1.6	0.15	46.0 ± 1.4	1.4 ± 1.1
	0.5	45.2	2.3	0.5	47.9 ± 2.7	2.3 ± 0.2
	1.0	47.4	3.8	1.0	48.2 ± 1.3	3.6 ± 1.2
NaCl	0.15	47.1	0.3			
	0.5	49.7	2.2			
	1.0	47.6	4.3			
$CaCl_2$	0.15	46.3	2.3			
	0.5	48.8	2.5			
	1.0	49.5	2.8			

[a] $\Delta H^{\circ\prime}$ values in kJ mol^{-1}; $3\sigma(\Delta H_1^{\circ\prime}) = 0.4-1.5$; $3\sigma(\Delta H_2^{\circ\prime}) = 0.8-3$.

TABLE 4

Empirical parameters for eqn. (1)

Salt	T (°C)	log $K_1^{H\prime}$		log $K_2^{H\prime}$	log $K_1^{H\prime}$	
		C	D	C	L ($I=1$)	L ($I=0.1$)
$Et_4N(Br,I)$	10	0.51	−0.20	0.33	0.31	0.045
	25	0.735	−0.46	0.20	0.275	0.059
	40	0.74	−0.44	0.28	0.30	0.060
	50	0.54	−0.31	0.225	0.23	0.044
NaCl	10	0.51	−0.15	0.16	0.36	0.046
	25	0.525	−0.18	0.12	0.345	0.047
	40	0.17	+0.12	0.135	0.29	0.021
	50	−0.28	+0.53	0.045	0.25	−0.011
$CaCl_2$	10	0.04	0	0.01	0.04	0.004
	25	−0.14	+0.15	0.02	0.01	−0.009
	40	−0.36	+0.28	0.02	−0.08	−0.027
	50	−0.42	+0.34	−0.02	−0.08	−0.053

Et_4NI: $L(I=1) = 0.29 - 0.0015\,(T-25)$; $L(I=0.1) = 0.052$.
NaCl: $L(I=1) = 0.33 - 0.0028\,(T-25)$; $L(I=0.1) = 0.035 - 0.0014\,(T-25)$.
$CaCl_2$: $L(I=1) = -0.006 - 0.0034\,(T-25)$; $L(I=0.1) = -0.013 - 0.0014\,(T-25)$.

the errors associated with formation constants are rather high. Nevertheless, calculations performed with the computer program ES4EC [14] on the propagation of errors (from stability constants to formation percentages), showed reasonable confidence intervals for species concentrations and formation percentages, as reported in Table 6. From the dependence on temperature of formation constants we calculate ΔH° and ΔS° values reported in Table 7. The body of results of this work are consistent with the possibility of determining the complete speciation of systems containing aminoacids and alkali and alkaline earth cations. Nevertheless, the amount of data accumulated up to now is not sufficient to draw general conclusions,

TABLE 5

Overall formation constants at $I = 0$ mol l^{-1}

Species	log $\beta \pm 3\sigma$			
	10 °C	25 °C	40 °C	50 °C
$[Na(ala)]^0$	0.2 ±0.3	0.3 ±0.2	0.3 ±0.3	0.4 ±0.3
$[Na(ala)H]^+$	10.03±0.15	9.61±0.10	9.23±0.10	9.10±0.15
$[Et_4N(ala)]^0$	0.1 ±0.2	0.15±0.2	0.15±0.2	0.2 ±0.2
$[Ca(ala)]^+$	1.23±0.05	1.36±0.05	1.41±0.05	1.54±0.05
$[Ca(ala)H]^{2+}$	10.51±0.08	10.21±0.06	9.84±0.06	9.69±0.07
$[(ala)HCl]^-$	10.03±0.25	9.78±0.10	9.32±0.15	9.29±0.20
$[(ala)H_2Cl]^0$	12.87±0.25	12.55±0.15	12.14±0.15	11.97±0.20

TABLE 6

Some formation percentages (with respect to the ligand) with errors ($T = 25\,°C$)

Species	pH	Formation ($\% \pm 3\sigma$)	C_M [a]
$[Et_4N(ala)]^0$	8.5	2 ± 1	0.5
	9.5	14 ± 6	
	10.5	35 ± 10	
$[Ca(ala)]^+$	9	17 ± 2	0.1
	10	53 ± 3	
	9	11 ± 1	0.05
	10	37 ± 3	
$[Ca(ala)H]^{2+}$	2	5 ± 1	0.1
	4	16 ± 2	
	2	3 ± 0.5	0.05
	4	9 ± 1	
$[(ala)HX]^-$	7.5	25 ± 4	0.5

[a] C_M, concentration of the cation in mol l^{-1}; ligand concentration, 6 mmol l^{-1}.

TABLE 7

Thermodynamic parameters at $I = 0$ mol l^{-1} and $T = 25\,°C$ [a]

Reaction	$-\Delta G° \pm 3\sigma$	$\Delta H° \pm 3\sigma$	$\Delta S° \pm 3\sigma$
$Na^+ + ala^- = [Na(ala)]^0$	1.7 ± 1.1	7 ± 4	29 ± 14
$Na^+ + [(ala)H]^0 = [Na(ala)H]^+$	-1.4 ± 0.6	0 ± 2	-5 ± 7
$Et_4N^+ + ala^- = [Et_4N(ala)]^0$	0.9 ± 1.2	4 ± 4	16 ± 15
$Ca^{2+} + ala^- = [Ca(ala)]^+$	7.8 ± 0.3	12 ± 1	67 ± 5
$Ca^{2+} + [(ala)H]^0 = [Ca(ala)H]^{2+}$	2.0 ± 0.4	6 ± 2	27 ± 7
$X^- + [(ala)H]^0 = [(ala)HX]^-$	-0.4 ± 0.6	7 ± 3	22 ± 10
$X^- + [(ala)H_2]^+ = [(ala)H_2X]^0$	2.0 ± 0.9	2 ± 3	13 ± 10

[a] $\Delta G°$ and $\Delta H°$ in kJ mol^{-1}; $\Delta S°$ in J K^{-1} mol^{-1}.

particularly as concerns the dependence on temperature of formation constants and the stability ($K_1^{Et_4N}$) and the nature of tetraethylammonium complexes. Further studies on this subject are forthcoming.

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