STUDY OF THE COORDINATED SYSTEM Pb(II)–ALANINE–ALANINATE ION

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The polarographic method has been applied to the study of the mixed-coordinated system Pb(II)–alanine–alaninate ion in aqueous medium, $I = 1{\cdot}0\ \text{mol}\ \text{l}^{-1}$ ($NaClO_4$) and 25 ± 0·1°C. The formation of the complexes $[PbA]^{2+}$ ($\beta_{10} = 13{\cdot}2$), $[PbA_2]^{2+}$ ($\beta_{20} = 25$), $[PbA(A^-)]^+$ ($\beta_{11} = 1{\cdot}01 \,.\, 10^5$), $[Pb(A^-)]^+$ ($\beta_{01} = 3{\cdot}76 \,.\, 10^4$) and $[Pb(A^-)_2]$ ($\beta_{02} = 6{\cdot}74 \,.\, 10^7$) was observed.

Freeman[1] has shown the utility of the information obtained in the study of some simple complexes for understanding the structure of the active sites of carboxy-peptidase.

Likewise, diverse observations have led to the study of the formation of metal ion complexes of small molecular weight since this is the way in which metal ions are mobilized during prolonged periods of nutrition. The reliability of the stability constant values of simple and mixed complexes with simple aminoacids is also of importance since they represent the main form of administration in the nutritive mixture or the form of excretion. Thus, the reinvestigation of the coordinated system Zn(II)–cysteinate–hystidinate[2] has led to a reduction of the initial estimation of the daily dosage of zinc from 38 mg to 32 mg in some nutritive mixtures studied.

On the other hand, the studies of the coordinated systems metal ion–aminoacids have, almost generally, taken into account only the anion as ligand, disregarding the complexing nature of the neutral species. It was therefore thought worthwhile to undertake a systematic analysis of these systems considering the complexation of the metal ion by both species. In view of the above, we decided to study the coordinated systems metal ion-aminoacid.

In this work, we report on the analysis of the mixed coordinated system Pb(II)–alanine–alaninate ion which has been little studied[3–7] and of which only the formation of two complexes with the alaninate ion, $[Pb(A^-)]^+$ and $Pb(A^-)_2$, has been described. No formation of any complex with either neutral or mixed alanine has been detected.

The dispersion of the results proposed is evident, particularly for β_{02}, oscillating between excessively wide limits: $\beta_{01}(1{\cdot}20-14{\cdot}8)\,.\,10^4$ and $\beta_{02}(1{\cdot}38\ -\ 67{\cdot}6\ -\ 1\,349)\,.\,10^5$, which, in our opinion, cannot be totally justified by the different experimental conditions or by the use of weakly complexing inert electrolytes.

THEORETICAL

If the molecules of neutral alanine (A) and the alaninate ion (A^-) are regarded as possible ligands of Pb(II) and if we assume that only two ligands can be coordinated, the Schaap–McMasters F_{00} function[9] can be derived as follows:

$$F_{00} = \{1 + \beta_{10}[A] + \beta_{20}[A]^2\} + \{\beta_{01} + \beta_{11}[A]\}\,[A^-] + \{\beta_{02}\}\,[A^-]^2\,. \qquad (1)$$

The studies were carried out at constant pH but different total concentrations of amino acid (C_A), so that [A] and $[A^-]$ vary with (C_A).

It is evident that at high pH values the complexes with the anion will predominate since the anion concentration will be important and the stability constants of the complexes formed by the anion must be much greater than those of the neutral form.

At lower pH values, the high concentration of the neutral species with respect to that of the anionic one can be assumed to compensate greatly for its much lower stability constant, and its complexes with the metal cation under study can be determined.

Between the limits mentioned, the formation of the mixed coordinated species will be possible.

In any case, the fact should be taken into account that if the pH required is very low, the concentration of the protonated form may be high, affecting appreciably the ionic strength. This effect can be minimized by decreasing the total concentration of the aminoacid.

Likewise, in every case it will be necessary to work with concentrations of complexing forms of amino acid such that complexation with them will prevail appreciably over the formation of hydroxo-complexes.

With regard to the expression for K_{a2}, Eq. (1) transforms to

$$\begin{aligned} F_{00} = {} & 1 + \{([H^+]/K_{a2})\,\beta_{10} + \beta_{01}\}\,[A^-] + \\ & + \{([H^+]/K_{a2})^2\,\beta_{20} + ([H^+]/K_{a2})\,\beta_{11} + \beta_{02}\}\,[A^-]^2 \end{aligned} \qquad (2)$$

a relationship which at constant pH will reduce to

$$F_{00} = 1 + B'[A^-] + C'[A^-]^2\,, \qquad (3)$$

where, if $m = [H^+]/K_{a2}$, the B' and C' coefficients will be defined by:

$$B' = m\beta_{10} + \beta_{01} \qquad (4)$$

$$C' = m^2\beta_{20} + m\beta_{11} + \beta_{02} \qquad (5)$$

and can be calculated in the usual manner.

If the substitution is made in terms of [A] the expressions will be analogous

$$F_{00} = 1 + \{(K_{a2}/[H^+])\,\beta_{01} + \beta_{10}\}\,[A] + \\ + \{(K_{a2}/[H^+])^2\,\beta_{02} + (K_{a2}/[H^+])\,\beta_{11} + \beta_{20}\}\,[A]^2 \qquad (6)$$

$$F_{00} = 1 + B'[A] + C'[A]^2\,, \qquad (7)$$

where:

$$B' = m^{-1}\beta_{01} + \beta_{10} \qquad (8)$$

$$C' = m^{-2}\beta_{02} + m^{-1}\beta_{11} + \beta_{20} \qquad (9)$$

The knowledge of an appropriate number of values of the B' and C' coefficients would allow us to determine the stability constants of the species present in the medium.

EXPERIMENTAL

A Metrohm E506 polarograph with an E505 polarographic stand was used for recording the i–E curves. An Ag/AgCl/NaCl saturated Metrohm EA427 electrode and an EA285 Pt electrode were employed as the reference and auxiliary electrodes, respectively. The temperature was maintained at 25 ± 0·1°C and the drop time was set at 3 s. The ionic strength was held constant at $I = 1{\cdot}0\ \text{mol}\ l^{-1}$ by addition of $NaClO_4$. The pH measurements were carried out with a pHM 84 digital pH-meter and a Radiometer GK2401C combined electrode. Solution of lead perchlorate of reagent grade (Merck) was standardized complexometrically. Sodium perchlorate (Merck) and L-alanine (Sigma) were also of reagent grade. The values of the acidity constants[8] were $pK_{a1} = 2{\cdot}39$ and $pK_{a2} = 9{\cdot}84$.

Procedures

The five sets of experiments were carried out at constant pH varying the total concentration of alanine between the limits indicated in Table I. In every case, the plots in the absence of ligand were made at low pH (2·00–3·00).

RESULTS AND DISCUSSION

In all the solutions studied, the polarograms show good symmetry and regular outline. The discharge takes place by a two electron process. In the sets of experiments carried out at higher pH, slight deviations from reversibility can be observed, which do not hinder the determination of the reversible half-wave potentials, $E^{r}_{1/2}$, the increases of which for sets III, IV and V are indicated, together with the diffusion limiting currents and F_{ij} functions, in Tables II, III and IV.

Figures 1, 2 and 3 present the plots of the F_{ij} functions vs the concentration of the ligand indicated. In each case, Eq. (*7*) is confirmed. Adjusting by the least-squares method provides the values of B' and C' given in Tables V and VI.

The five sets of experiments were planned such that I and II correspond to low pH values, in which the complexes with neutral alanine should prevail. The sets carried out at higher pH values, (III–V), allow the determination of the simple and mixed complexes with the anionic form.

It will be shown that in Eqs (*8*) and (*9*) the summands other than β_{10} and β_{20} are negligible with respect to the corresponding coefficients, B' and C', which lets us to propose the following values of the formations constants of the complexes $[PbA]^{2+}$ and $[PbA_2]^{2+}$: $\beta_{10} = 13{\cdot}2 \pm 0{\cdot}4$ and $\beta_{20} = 25 \pm 2$.

As can be observed for the sets II, the plot of F_{00} vs $[A]$ is a straight line, indicating that it fits the equation $F_{00} = 1 + B'[A]$.

The absence of the quadratic term is due to the fact that the concentration of alanine was very low in this study, so that $C'[A]^2$ was negligible. The value obtained for β_{10} in the sets II, $15{\cdot}5 \pm 1{\cdot}2$, is in a very good agreement with that determined previously, viz. 13·2.

With the β_{10} values known, from Eq. (*4*) the following values of β_{01} were obtained: $(\beta_{01})_{III} = 2{\cdot}78 . 10^4$, $(\beta_{01})_{IV} = 3{\cdot}75 . 10^4$, $(\beta_{01})_{V} = 4{\cdot}75 . 10^4$, which are mutually consistent and allow us to determine the constant $\beta_{01} = (3{\cdot}8 \pm 1{\cdot}0) . 10^4$ for the $[Pb(A^-)]^+$ complex.

Taking into account Eq. (*5*) in which β_{20} is known, the plot of the function $C_{[A^-]} - m^2\beta_{20} = \beta_{02} + m\beta_{11}$ vs m will be a straight line with the intercept β_{02}

TABLE I

Conditions for sets of experiments

Set	pH	$C_A . 10^2$ mol l^{-1}	$[A^-]$ mol l^{-1}	$[A]$ mol l^{-1}
I	3·16	5·0—38·0	(0·88—6·62) . 10^{-8}	0·0426—0·3167
II	3·18	0·5—3·8	(9·36—70·5) . 10^{-10}	(4·28—32·2) . 10^{-3}
III	6·67	5·0—15·0	(3·43—10·0) . 10^{-5}	0·049—0·1488
IV	6·75	5·0—15·0	(3·96—11·8) . 10^{-5}	0·0498—0·1482
V	7·00	5·0—38·0	(7·16—53·8) . 10^{-5}	0·0496—0·3720

and the slope β_{11}. Figure 4 shows the above-mentioned dependence, which gives the formation constants of the complexes $[Pb(A^-)_2]$ and $[Pb(A)(A^-)]^+$ of β_{02} = 6·74.

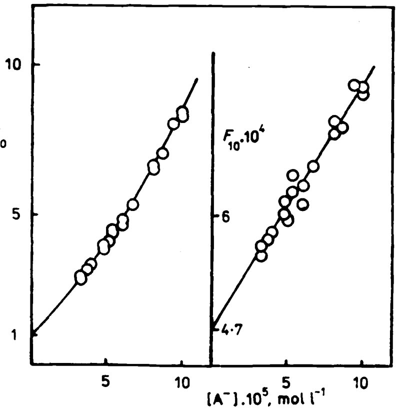

Fig. 1

Plot of the functions F_{00} and F_{10} vs $[A^-]$ at pH 6·67

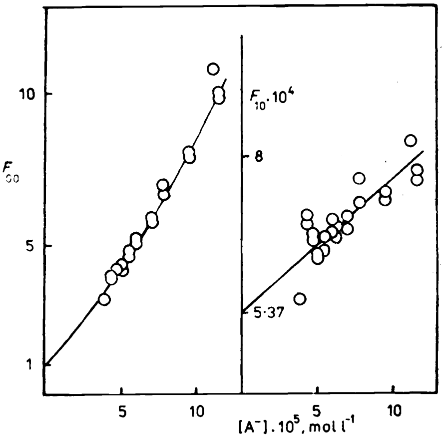

Fig. 2

Plot of the functions F_{00} and F_{10} vs $[A^-]$ at pH 6·75

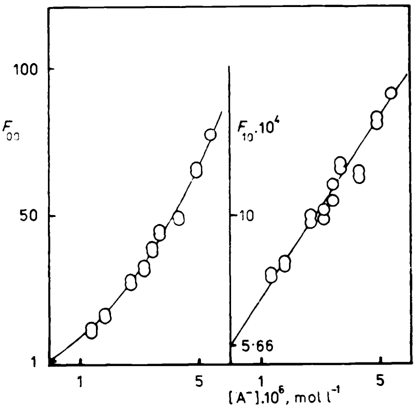

Fig. 3

Plot of the functions F_{00} and F_{10} vs $[A^-]$ at pH 7·00

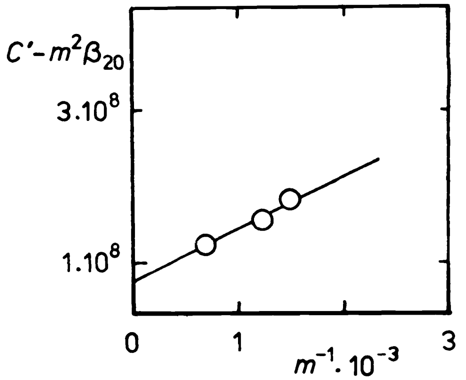

Fig. 4

Plot of C'-$m^2\beta_{20}$ vs m^{-1}

. $10^7 \pm 0{\cdot}7$ and $\beta_{11} = 1{\cdot}01 \,.\, 10^5 \pm 0{\cdot}1$. This is the first experimental confirmation of the stabilization of the complexes $[PbA]^{2+}$, $[PbA_2]^{2+}$ and $[Pb(A^-)]^+$.

A comparison is only possible with the theoretical value from the Watters[10] equations using the constants of the simple complexes and from purely statistical considerations: $\beta_{11} = 2\beta_{20}^{1/2}\beta_{02}^{1/2} = 0{\cdot}821 \,.\, 10^5$. This is in a remarkable agreement with the experimental value, $\beta_{11} = 1{\cdot}01 \,.\, 10^5$.

The constants of the simple coordinated species with the alaninate ion, $\beta_{01} = 3{\cdot}8 \,.\, 10^4$ and $\beta_{02} = 6{\cdot}74 \,.\, 10^7$, fall within the range of values reported in the literature.

TABLE II

Analysis of the system Pb(II)–alanine–alaninate ion-$NaClO_4$ in aqueous medium. $E^{r}_{1/2}$ of Pb^{2+} in 1M $NaClO_4$: −341 mV, i_d = 136 mm, $[Pb^{2+}] = 1 \,.\, 10^{-4}$ mol l^{-1}

$C_A \,.\, 10^2$ mol l^{-1}	pH	$[A^-] \,.\, 10^5$ mol l^{-1}	i_d mm	$\Delta E_{1/2}$ mV	F_{00}	$F_{10} \,.\, 10^{-3}$
5·0	6·68	3·43	122	12·5	2·9627	57·222
				12·4	2·9397	56·552
5·5	6·67	3·70	123	13·5	3·1765	58·225
6·0	6·67	4·00	124·1	14·3	3·3507	58·776
				14·3	3·3507	58·776
7·0	6·68	4·82	121·3	16	3·9130	60·436
				16·2	3·9744	61·710
7·5	6·67	5·03	122·5	16·4	3·9973	59·588
				16·4	3·9973	59·588
8·0	6·67	5·38	121·8	17·8	4·4831	64·742
				17·5	4·3796	62·819
9·0	6·67	6·06	122·6	18·9	4·8521	63·565
				18·5	4·7033	61·111
10·0	6·67	6·72	121·5	20·2	5·4174	65·735
12·0	6·67	8·07	121·1	22·5	6·7066	70·714
				22·7	6·6030	69·430
13·0	6·67	8·68	120·2	23·5	7·0799	70·045
				23·5	7·0799	70·045
14·0	6·67	9·42	120·5	25·2	8·0616	74·964
				25·2	8·0616	74·964
15·0	6·67	10·0	119	25·7	8·4872	74·872
				25·6	8·4214	74·214

Our values are slightly lower than those obtained by Maeda et al.[3] in 3M $NaClO_4$ and higher than those determined polarographically by Dao et al.[4] in 1M KNO_3; this is not unexpected in view of the weakly complexing nature of the NO_3^- ion.

Let us now discuss the influence of the above-mentioned complexing effect by applying the method proposed by Rodríguez Placeres and coworkers[11]. Since the function obtained by adjusting the ionic strength to 1 mol l^{-1} with nitrates is actually

TABLE III

Analysis of the system Pb(II)–alanine–alaninate ion-$NaClO_4$ in aqueous medium. $E^r_{1/2}$ of Pb^{2+} in 1M $NaClO_4$: −341 mV, i_d = 129·5 mm, $[Pb^{2+}] = 1 . 10^{-4}$ mol l^{-1}

$C_A . 10^2$ mol l^{-1}	pH	$[A^-] . 10^5$ mol l^{-1}	i_d mm	$\Delta E_{1/2}$ mV	F_{00}	$F_{10} . 10^{-3}$
5·0	6·74	3·956	120·3	14·1	3·2262	56·269
				14·1	3·2262	56·269
5·5	6·74	4·352	119·2	16·9	4·0490	70·059
				16·7	3·9864	68·622
6·0	6·75	4·834	121·2	17·6	4·2052	66·307
				17·7	4·2380	66·987
6·5	6·74	5·117	120·3	17·7	4·2697	63·893
				17·6	4·2366	63·246
7·0	6·75	5·634	120·2	18·7	4·6192	64·243
				19·1	4·7651	66·836
7·5	6·75	6·091	121·4	20·4	5·2207	69·294
				20·1	5·1002	67·316
8·0	6·74	6·349	119·9	20·5	5·3273	68·154
				20·3	5·2450	66·858
9·0	6·74	7·086	118·2	21·7	5·9331	69·618
				21·4	5·7961	67·686
10·0	6·74	7·897	120·5	23·5	6·6952	72·120
				24·1	7·0154	76·174
12·0	6·75	9·619	119·6	25·7	8·0057	72·832
				25·9	8·1313	74·138
14·0	6·75	11·320	119·3	29	10·376	82·795
				29	10·376	82·795
15·0	6·74	11·770	119 2	28·7	10·145	77·676
				28·5	9·9888	76·345

the quantity R_0, defined as

$$R_0 = 1 + \frac{-3\beta_{001} - 6\beta_{002} + \beta_{010} + \beta_{011}}{1 + \beta_{001} + \beta_{002}}[\mathrm{A}^-] + \frac{9\beta_{002} - 3\beta_{011} + \beta_{020}}{1 + \beta_{001} + \beta_{002}}[\mathrm{A}^-]^2 \tag{10}$$

$$R_0 = 1 + B'[\mathrm{A}^-] + C'[\mathrm{A}^-]^2 \tag{11}$$

and the constants of the complexes $[\mathrm{Pb(NO_3)}]^+$ and $\mathrm{Pb(NO_3)_2}$ are known[12] ($\beta_{001} = 2{\cdot}1$ and $\beta_{002} = 2{\cdot}1$), the value of β_{011} can be determined from the Watters equation and the knowledge of β_{010} and β_{020} thus becomes feasible since according to Dao et al.[6] $B' = 1{\cdot}51 \,.\, 10^4$ and $C' = 6{\cdot}75 \,.\, 10^6$. Hence, $\beta_{010} = 5{\cdot}473 \,.\, 10^4$, $\beta_{020} = 3{\cdot}508 \,.\, 10^7$.

TABLE IV

Analysis of the system Pb(II)–alanine–alaninate ion-$\mathrm{NaClO_4}$ in aqueous medium. $E^{\mathrm{r}}_{1/2}$ of $\mathrm{Pb^{2+}}$ in 1M $\mathrm{NaClO_4}$: −341 mV, i_d = 140·6 mm, $[\mathrm{Pb^{2+}}] = 1 \,.\, 10^{-4}$ mol l^{-1}

$C_\mathrm{A} \,.\, 10^2$ mol l^{-1}	pH	$[\mathrm{A}^-] \,.\, 10^5$ mol l^{-1}	i_d mm	$\Delta E_{1/2}$ mV	F_{00}	$F_{10} \,.\, 10^{-3}$
10	7·0	14·3	121·2	30·6	12·560	80·841
				30·4	12·366	79·484
13	7·0	18·5	119·9	34	16·543	84·019
				34·2	16·803	85·422
19	7·0	27·2	118	40·6	28·099	99·630
				40·4	27·665	98·035
22	7·0	31·5	118·6	42·8	33·180	102·16
				42·4	32·162	98·929
24	7·0	34·5	117·5	44·8	39·132	110·53
				44·2	37·347	105·35
26	7·0	37·4	117·4	46·4	44·361	115·94
				46·6	45·051	117·80
30	7·0	42·9	115·5	47·6	49·505	113·07
				47·8	50·282	114·88
34	7·0	48·7	114·8	51	64·899	131·21
				51·2	65·918	133·30
38	7·0	53·8	113·1	53	76·972	141·21
				53	76·972	141·21

TABLE V

Coefficients of the polynomial $F_{00} = 1 + B'[A] + C'[A]^2$

Set	$m \,.\, 10^{-6}$	B'	C'
I	4·786	13·2	25·0
II	4·571	15·5	—

TABLE VI

Coefficients of the polynomial $F_{00} = 1 + B'[A^-] + C'[A^-]^2$

Set	$m \,.\, 10^{-3}$	$B' \,.\, 10^{-4}$	$C' \,.\, 10^{-8}$
III	1·479	4·735 ± 0·084	2·756 ± 0·12
IV	1·230	5·378 ± 0·21	2·222 ± 0·28
V	0·692	5·660 ± 0·3	1·513 ± 0·073

TABLE VII

Stability constants of Pb(II) and Cd(II) complexes

Ion	β_{10}	β_{20}	$\beta_{01} \,.\, 10^{-4}$	$\beta_{02} \,.\, 10^{-7}$	$\beta_{11} \,.\, 10^{-5}$
Cd^{2+}	7·3	14	1·15	2·7	1·7
Pb^{2+}	13·2	25·0	3·76	6·74	1·01

In Table VII, the constants obtained in this work are compared with those previously determined for the coordinated system Cd(II)–alanine–alaninate ion[13].

A marked parallelism can be observed in the values of the different constants, except for the mixed complex $MA(A^-)$. The constants of the Pb^{2+} complexes are $2-3$ times higher than those of their Cd^{2+} equivalents.

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