STUDY OF THE COORDINATED SYSTEM Cd(II)–VALINE–VALINATE ION

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The polarographic method has been applied to the study of the coordinated systems Cd(II)–neutral valine and Cd(II)–valinate ion in aqueous medium and I = 1.0 mol l^{-1} ($NaClO_4$). The stability constants of the complexes were determined as: $[Cd(HV)]^{2+}$ ($\beta_{10} = 7 \pm 0.5$), $[Cd(HV)_2]^{2+}$ ($\beta_{20} = 24 \pm 4$), $[Cd(HV)_3]^{2+}$ [$\beta_{30} = (1.5 \pm 0.32) \cdot 10^2$], $[Cd(V^-)]^+$ [$\beta_{01} = (4.1 \pm 0.3) \cdot 10^3$], $[Cd(V^-)_2]$ [$\beta_{02} = (1.3 \pm 0.2) \cdot 10^7$], $[Cd(V^-)_3]^-$ [$\beta_{03} = (1.5 \pm 0.3) \cdot 10^9$], $[Cd(HV)(V^-)]^+$ [$\beta_{11} = (4.3 \pm 0.8) \cdot 10^4$], $[Cd(HV)(V^-)_2]$ [$\beta_{12} = (1.7 \pm 0.3) \cdot 10^7$] and $Cd(HV)_2(V^-)]^+$ [$\beta_{21} = (1.2 \pm 0.3) \cdot 10^5$].

In an earlier work[1] we commented on the importance of studying the coordinated systems metal ion–amino acids and on the usefulness of a method that allows all the complexes existing in the medium with the neutral and anionic forms of the amino acid to be revealed, as well on the non-advisability of using inert electrolytes that are weakly complexing the metal ion under study.

In the present work we report on the study of the coordinated system Cd(II)–neutral valine–valinate ion, which has only been partially studied, since the coordination with neutral valine, or the mixed complexes with this ligand and its anionic form have not been analysed. The complexes of the valinate ion with Cd^{2+} have received a good deal of attention, different methods, including the polarographic one, having been applied to their study. In a general manner, coordinated species with one or two valinate ligands can be identified. Only four works, three of them in KNO_3, mention the existence of the complex $[Cd(V^-)_3]^-$.

The dispersion of the results is quite remarkable with the complexes $[Cd(V^-)]^+$ and $[Cd(V^-)_2]$, and cannot be justified only by the different experimental conditions used or by the weakly complexing nature of most of the inert electrolytes employed in adjusting the ionic strength of the medium. The constants proposed until now[2-8] range between the following limits:

$$\beta_{01} = (2.88 - 20.9) \cdot 10^3$$
$$\beta_{02} = (2.88 - 31.0) \cdot 10^6$$
$$\beta_{03} = (3.02 - 7.94) \cdot 10^8$$

THEORETICAL APPROACH

When an amino acid, for example valine, behaves like a dibasic substance in solution, the neutral (HV), protonated (H_2V^+) and anionic (V^-) forms of the corresponding amino acid will be found to be in equilibrium:

$$H_2V^+ \overset{K_{a1}}{\rightleftharpoons} H^+ + HV \overset{K_{a2}}{\rightleftharpoons} 2H^+ + V^-$$

The concentration of each of the species in solution depends on the total concentration of amino acid, c_V, on the values of their acidity constants and on the pH of the medium and is calculated from the corresponding distribution function. In view of the foreseeable complexing nature of the neutral and anionic forms of the amino acid in the presence of a metallic cation, the formation of simple and mixed complexes with these ligands is to be expected. The F_{00} function of Schaap and McMasters[9] will therefore develop as follows:

$$\begin{aligned} F_{00} = {} & \{1 + \beta_{01}[V^-] + \beta_{02}[V^-]^2 + \beta_{03}[V^-]^3\} + \\ & + \{\beta_{10} + \beta_{11}[V^-] + \beta_{12}[V^-]^2\}\,[HV] + \\ & + \{\beta_{20} + \beta_{21}[V^-]\}\,[HV]^2 + \beta_{30}[HV]^3 \end{aligned} \qquad (1)$$

It is evident that at high pH values the complexes with the anion will predominate, since their concentration will be significant and the stability constants will be higher than those of the neutral form.

At very low pH values, it is to be expected that the high concentration of the neutral form with respect to that of the anionic form compensates greatly for its much lower stability constant and that complexes formed with the metal ion under study can be determined. At intermediate pH values, the calculation of the constants of the mixed complexes with the neutral and anionic species should be feasible. In any case, it must be taken into account that if the pH is very low, the concentration of the protonated form can be high and may modify the ionic strength. This effect can be minimized by decreasing the total concentration of amino acid present in the medium. Similarly, in every case the concentration of complexing forms of amino acid used must lead to complexes that predominate greatly over the species coordinated with the hydroxyl ion always present in the medium.

In the studies performed at constant pH, when the total concentration of amino acid varies it is evident that both [HV] and $[V^-]$ will change and that at any pH:

$$[HV] = m\,[V^-]\,, \quad \text{where } m = [H^+] / K_{a2}\,. \qquad (2)$$

If we wish to study the complexes with the anionic form we must substitute in Eq. (*1*) the value of [HV] obtained from Eq. (*2*), hence

$$F_{00} = 1 + \{m\beta_{10} + \beta_{01}\}\,[V^-] + \\ + \{m^2\beta_{20} + m\beta_{11} + \beta_{02}\}\,[V^-]^2 + \\ + \{m^3\beta_{30} + m^2\beta_{21} + m\beta_{12} + \beta_{03}\}\,[V^-]^3 . \tag{3}$$

The relationship at constant pH becomes

$$F_{00} = 1 + B'\,[V^-] + C'\,[V^-]^2 + D'\,[V^-]^3 . \tag{4}$$

In order to calculate the species coordinated with the neutral form, in Eq. (*1*) the value of $[V^-]$ determined from Eq. (*2*) will be substituted and the following expression obtained:

$$F_{00} = 1 + \{m^{-1}\beta_{01} + \beta_{10}\}\,[HV] + \\ + \{m^{-2}\beta_{02} + m^{-1}\beta_{11} + \beta_{20}\}\,[HV]^2 + \\ + \{m^{-3}\beta_{03} + m^{-2}\beta_{12} + m^{-1}\beta_{21} + \beta_{30}\}\,[HV]^3 \tag{5}$$

a relationship which at constant pH becomes:

$$F_{00} = 1 + B'\,[HV] + C'\,[HV]^2 + D'\,[HV]^3 , \tag{6}$$

where B', C' and D' represent the arrangements given in Eq. (*5*) and can be calculated in the usual way. However, if working at variable pH, an initial solution will be used in such a manner that the concentrations of the different forms of the amino acid will change upon varying the pH. At a sufficiently high pH, where the concentration of $[H_2V^+]$ is negligible, the sum of the concentrations of the neutral and negative species will be found to equal the total concentration of amino acid, that is:

$$c_V = [HV] + [V^-] . \tag{7}$$

In order to calculate the constants for the anionic form, the value of [HV] in Eq. (*1*) will be that obtained from Eq. (*7*), giving:

$$F_{00} = \{1 + \beta_{10}c_V + \beta_{20}c_V^2 + \beta_{30}c_V^3\} + \\ \{-\beta_{10} - 2\beta_{20}c_V - 3\beta_{30}c_V^2 + \beta_{01} + \beta_{11}c_V + \beta_{21}c_V^2\}\,[V^-] + \\ \{\beta_{20} + 3\,\beta_{30}c_V - \beta_{11} - 2\,\beta_{21}c_V + \beta_{02} + \beta_{12}c_V\}\,[V^-]^2 + \\ \{-\beta_{30} + \beta_{21} - \beta_{12} + \beta_{03}\}\,[V^-]^3 \tag{8}$$

the terms in brackets being constant, and therefore:

$$F_{00} = A' + B'\,[V^-] + C'\,[V^-]^2 + D'\,[V^-]^3 . \tag{9}$$

A similar expression would be obtained for the determination of the species coordinated with the neutral form of the amino acid. The knowledge of an appropriate number

of values of the B', C' and D' coefficients would allow us to determine the stability constants of the species present in the medium.

EXPERIMENTAL

Each of the i–E curves was plotted as a normal pulse polarogram with a Metrohm E506 polarograph with an E505 polarographic stand. Pt (EA285) and Ag/AgCl/NaCl, sat. Metrohm EA427 electrodes were used as counter and reference electrodes, respectively, and the working electrode was DME. The temperature in the cell was 25 ± 0.05 °C. The ionic strength was adjusted to I = 1.0 mol l^{-1} with $NaClO_4$. Measurements of pH were carried out with a pHM84 digital potentiometer Radiometer with a GK 2401C Radiometer combined electrode. Drop time was controlled at 3.0 s. The concentration of Cd^{2+} ion was 7 . 10^{-5} mol l^{-1} in the studies at constant pH and 1.7 . 10^{-5} mol l^{-1} at variable pH. The sodium perchlorate and cadmium sulfate were Merck products of p.a. quality, the L-valine was from Sigma and the sodium hydroxide used for adjusting the pH was also of p.a. quality from May and Baker. The values of the acidity constants[10] were: pK_{a1} = 2.35 and pK_{a2} = 9.62.

RESULTS AND DISCUSSION

Of the six studies performed, four were carried out at constant pH and varying the total concentration of valine between the limits indicated, and the remaining two at variable pH, as can be seen in Table I.

In all the systems studied, the plots of log $[(\bar{i}_d - \bar{i})/\bar{i}]$ vs $-E$ show that the discharge takes place by a reversible two electron process. The values of the reversible half-wave potentials were obtained from these plots. Tables II, III and IV show $\Delta E_{1/2}$ the diffusion limiting currents and the F_{ij} functions for studies II, IV and V.

Adjusting F_{10} as a second-degree polynomial function provides the values of the coefficients B', C' and D' given in Table V. The value of the coefficient A' in the studies carried out at variable pH was set equal to 2.1, obtained from the data for β_{i0} derived from experiments I and II.

TABLE I
Experimental conditions for Cd(II)–valine–$NaClO_4$ system

Set	pH	c_V . 10^2, mol l^{-1}	$[V^-]$, mol l^{-1}	[HV], mol l^{-1}
		Constant pH		
I	2.88	2.0 – 24.0	(2.655 – 33.79) . 10^{-9}	(15.25 – 185.5) . 10^{-3}
II	2.99	3.0 – 28.0	(5.657 – 45.26) . 10^{-9}	(24.26 – 222.0) . 10^{-3}
III	9.07	1.5 – 16.0	(3.796 – 29.82) . 10^{-3}	(11.22 – 130.2) . 10^{-3}
IV	9.14	1.0 – 24.0	(2.574 – 62.85) . 10^{-3}	(7.425 – 177.2) . 10^{-3}
		Variable pH		
V	7.01 – 8.67	10.0 – 9.80	(2.449 – 98.86) . 10^{-4}	99.75 – 88.11
VI	7.37 – 8.50	10.0 – 9.80	(5.592 – 69.10) . 10^{-4}	99.44 – 91.09

Studies I and II correspond to low values of pH, at which the complex with neutral valine must significantly prevail. In those performed at high pH, III and IV, the complexes with valinate were present in excess. Lastly, the pH range of studies V and VI was chosen such that the mixed coordinated species could be present at appreciable concentrations.

TABLE II
Analysis of the Cd(II)–neutral valine–$NaClO_4$ system in aqueous medium by Schaap and McMasters method ($c(NaClO_4)$ = 1 mol l^{-1}, $-E^*_{1/2}$ = 527.8 mV, $\bar{i}_d$ = 130.1 mm, sensitivity = 6 . 10^{-9} A mm^{-1})

c_V . 10^2 mol l^{-1}	pH	[HV] . 10^3 mol l^{-1}	$\bar{i}_d$, mm	$\Delta E^*_{1/2}$, mV	F_{00}	F_{10}
3.0	2.98	24.26	130.8	2.3	1.1897	7.8194
4.0	2.99	32.50	129.4	2.7	1.2406	7.4030
				2.9	1.2600	8.0000
5.0	2.98	40.45	129.8	3.5	1.3162	7.8171
				3.7	1.3369	8.3289
6.0	2.98	48.54	127.3	4.5	1.4507	9.2851
				4.3	1.4283	8.8236
7.0	2.98	56.81	127.3	4.9	1.4966	8.7414
				5.1	1.5201	9.1551
8.0	2.99	64.95	127.8	5.5[a]	1.5621	8.6543
10.0	2.99	81.22	125.9	7.1	1.7959	9.7993
				7.3	1.8241	10.146
12.0	2.99	97.76	125.6	8.1[a]	1.9459	9.6757
14.0	3.00	114.7	124.0	10.1	2.3031	11.361
				9.9	2.2675	11.051
16.0	3.01	131.9	124.6	11.3[a]	2.5164	11.497
18.0	2.97	145.2	122.7	12.7	2.8496	12.738
				13.1	2.9398	13.359
20.0	2.99	162.9	121.8	14.7[a]	3.3543	14.452
22.0	2.99	179.1	121.6	15.7[a]	3.6318	14.694
24.0	2.96	192.3	121.3	18.1[a]	4.3887	17.622
28.0	2.93	222.0	116.8	18.7	4.7757	17.008
				18.5	4.7020	16.676

[a] From two identical measurements.

TABLE III
Analysis of the Cd(II)–ion valinate–$NaClO_4$ system in aqueous medium by Schaap and McMasters method ($c(NaClO_4)$ = 1 mol l^{-1}, $-E^r_{1/2}$ = 527.8 mV, $\bar{i}_d$ = 129.2 mm, sensitivity = 6 . 10^{-9} A mm^{-1})

c_V . 10^2 mol l^{-1}	pH	$[V^-]$. 10^3 mol l^{-1}	$\bar{i}_d$, mm	$\Delta E^r_{1/2}$, mV	F_{00} . 10^{-2}	F_{10} . 10^{-3}
1.0	9.16	2.574	110.5	60.3[a]	1.2779	49.258
1.5	9.14	3.731	110.7	69.3	2.5704	68.625
				69.5	2.6107	69.705
2.0	9.15	5.061	109.9	77.7[a]	4.9788	98.178
2.5	9.32	8.346	108.0	92.9	16.542	198.08
				93.3	17.062	204.55
3.0	9.20	8.263	106.2	93.5[a]	17.626	213.19
4.0	9.13	9.779	110.5	98.3	24.615	251.61
				98.9	25.792	263.65
5.0	9.17	13.09	97.3	108.5[a]	61.843	472.37
6.0	9.14	14.93	103.3	112.5	79.531	532.63
				112.9	82.046	549.67
7.0	9.10	16.24	104.9	115.9	102.04	628.26
				116.3	105.27	648.15
8.0	9.10	18.56	108.8	119.7	132.25	712.50
				120.1	136.44	735.08
10	9.05	21.21	105.7	124.7	200.91	947.20
				124.5	197.81	932.58
12	9.12	28.83	105.2	134.7	439.69	1525.1
				134.9	446.59	1549.0
14	9.10	32.47	103.5	139.1	629.48	1938.6
				138.6	619.18	1879.2
16	9.13	39.12	103.3	145.3[a]	1021.9	2612.3
18	9.13	44.01	103.3	150.9	1580.6	3590.9
				150.7	1555.9	3535.4
20	9.18	53.27	101.9	155.9	2364.4	4438.5
				155.3	2256.5	4235.9
22	9.16	56.64	103.8	158.3	2797.9	4939.8
				158.7	2886.4	5096.1
24	9.17	62.85	103.2	163.1[a]	4089.1	6506.1

[a] From two identical measurements.

Determination of the Constants for the Neutral Form, β_{i0}

The B', C' and D' coefficients are defined by the equations given in expression (*5*). Since the stability constants of the complexes with the valinate ion or of the mixed complexes were unknown, we considered the most unfavourable value indicated by the B', C' and D' coefficients obtained in the studies at high pH, which by definition (*3*) are greater. As values of the constants for the mixed complexes we have taken those calculated by applying the Watters equations[11], taking as β_{i0} and β_{0j} the limits obtained from the B', C' and D' coefficients at low and high pH, respectively.

Upon substituting in expression (*5*) the values obtained (studied I and II), the summands other than β_{i0} are negligible with respect to the values obtained for the

TABLE IV
Analysis of the Cd(II)–ion valinate–$NaClO_4$ system in aqueous medium by Schaap and McMasters method ($c(NaClO_4)$ = 1 mol l^{-1}, $-E^r_{1/2}$ = 527.8 mV, $\bar{i}_d$ = 66.7 mm, sensitivity = 2.5 . 10^{-9} A mm^{-1})

c_V . 10 mol l^{-1}	pH	[HV] . 10^4 mol l^{-1}	$\bar{i}_d$, mm	$\Delta E^r_{1/2}$, mV	F_{00}	F_{10} . 10^{-2}
1.0	7.37	5.592	61.3	29.8	11.070	160.40
1.0	7.69	11.61	60.8	43.2	31.675	254.73
				43.4	32.172	259.01
0.99	7.77	13.79	61.5	48.0	45.501	314.72
				47.6	44.106	304.61
0.99	7.54	16.16	59.9	51.2[a]	59.932	357.87
0.99	7.98	22.17	60.4	58.8	107.40	474.96
				58.6	105.74	467.47
0.99	8.08	27.75	59.3	64.4	169.18	602.09
				64.2	166.54	592.57
0.99	8.15	32.45	60.5	68.0	219.43	669.73
				69.2	240.92	735.96
0.99	8.24	39.62	60.1	73.6	341.59	856.86
				73.8	346.95	870.39
0.99	8.35	50.46	59.0	80.2	581.64	1148.5
				80.4	590.77	1166.6
0.98	8.44	60.74	60.2	85.6	867.91	1425.4
				86.0	895.36	1470.6
0.98	8.50	69.10	59.0	89.8[a]	1228.0	1774.2

[a] From two identical measurements.

coefficients. Considering the good agreement between the data for the coefficients, we propose as the best the mean values of the formation constants:

$$\beta_{10} = 7 \pm 0.5,\ \beta_{20} = 24 \pm 4 \text{ and } \beta_{30} = 146 \pm 32 .$$

Determination of the Constants for the Anionic Form, β_{0j}

In this case the coefficients are given by expression (*3*). Similar to the above case, for studies III and IV all the summands other than β_{0j} are negligible with respect to the values of their corresponding coefficients, and the following mean values are obtained:

$$\beta_{01} = (4.1 \pm 0.3) \cdot 10^3,\ \beta_{02} = (1.3 \pm 0.2) \cdot 10^7 \text{ and } \beta_{03} = (1.5 \pm 0.3) \cdot 10^9 .$$

Determination of the Constants β_{ij}

These values were obtained from the data at variable pH, expression (*8*). The values obtained in studies V and VI are taken as those of the *B'*, *C'* and *D'* coefficients. As can be seen in the equations defining the *B'*, *C'* and *D'* coefficients, in each of them are present more than one of our unknowns β_{11}, β_{21} and β_{12}. Each of the summands is therefore evaluated in order to determine those which are negligible with respect to the remainder, thus identifying the most significant constants. With the summands referring to mixed complexes, we shall consider as the initial value that calculated by means of the Watters equations:

$$\beta_{11} = 3.533 \cdot 10^4,\ \beta_{12} = 2.070 \cdot 10^7 \text{ and } \beta_{21} = 9.522 \cdot 10^4 .$$

TABLE V
Coefficients of the polynomial function F_{00}

Set	pH	*m*	*B'*	*C'*	*D'*
			Constant pH		
I	2.88	$5.495 \cdot 10^6$	7.016	24.09	$1.779 \cdot 10^2$
II	2.99	$4.226 \cdot 10^6$	7.054	23.85	$1.135 \cdot 10^2$
III	9.07	3.548	$4.066 \cdot 10^3$	$1.121 \cdot 10^7$	$1.699 \cdot 10^9$
IV	9.14	3.020	$4.043 \cdot 10^3$	$1.478 \cdot 10^7$	$1.354 \cdot 10^9$
			Variable pH		
V	7.02 – 8.67		$10.18 \cdot 10^3$	$1.548 \cdot 10^7$	$1.427 \cdot 10^9$
VI	7.37 – 8.50		$8.813 \cdot 10^3$	$1.384 \cdot 10^7$	$1.482 \cdot 10^9$

By substituting the values in the equation that defines D' (Eq. (*8*)) it is seen that all the remaining summands are negligible with respect to that corresponding to the complex $[Cd(V^-)_3]^-$. The perfect agreement between the two values of the coefficient, as well as their mean value $1.5 \cdot 10^9$, fully ratify the value proposed by us for β_{03}.

The good concordance between the two values of C' found supports the validity of their mean value:

$$C' = 1.466 \cdot 10^7 .$$

A comparative evaluation of the summands of the equation that defines C' reveals that only $\beta_{12} c_V$ and β_{02} are significant.

$$C' \approx \beta_{02} + \beta_{12} c_V, \text{ hence } \beta_{12} = (1.7 \pm 0.3) \cdot 10^7 .$$

The similarity between the values of B' is also noteworthy, and their mean value is therefore taken as being representative:

$$B' \approx 9.497 \cdot 10^3 .$$

In the definition equation the terms to be taken into account are:

$$B' = \beta_{01} + \beta_{11} c_V + \beta_{21} c_V^2 . \qquad (10)$$

For the determination of the constants of the complexes $[Cd(HV)(V^-)]^+$ and $[Cd(HV)_2(V^-)]^+$ it will be considered that the relation between them is established by the Watters equations:

$$\frac{\beta_{21}}{\beta_{11}} = 2.695 .$$

Substituting this relation in Eq. (*10*), we obtain

$$\beta_{11} = (4.3 \pm 0.8) \cdot 10^4 \text{ and } \beta_{21} = (1.2 \pm 0.3) \cdot 10^5 .$$

It should be pointed out that this is the first time this coordinated system has been studied fully, to reveal the existence of the following complexes: $[Cd(HV)]^{2+}$ ($\beta_{10} = 7 \pm 0.5$), $[Cd(HV)_2]^{2+}$ ($\beta_{20} = 24 \pm 4$), $[Cd(HV)_3]^{2+}$ [$\beta_{30} = (1.5 \pm 0.32) \cdot 10^2$], $[Cd(V^-)]^+$ [$\beta_{01} = (4.1 \pm 0.3) \cdot 10^3$], $[Cd(V^-)_2]$ [$\beta_{02} = (1.3 \pm 0.2) \cdot 10^7$], $[Cd(V^-)_3]^-$ [$\beta_{03} = (1.5 \pm 0.3) \cdot 10^9$], $[Cd(HV)(V^-)]^+$ [$\beta_{11} = (4.3 \pm 0.8) \cdot 10^4$], $[Cd(HV)(V^-)_2]$ [$\beta_{12} = 1.7 \pm 0.3) \cdot 10^7$] and $[Cd(HV)_2(V^-)]^+$ [$\beta_{21} = (1.2 \pm 0.3) \cdot 10^5$] .

The fact that the existence of coordinated species with more than three ligands has not been detected in any of the cases provides further evidence for the bidentate nature of neutral valine and of the valine ion. With regard to the coordinated species with the

valinate ion, the fact that the existence of a stable complex $[Cd(V^-)_3]^-$ was revealed should be emphasized.

The data for β_{01} and β_{02} fall within the range of values reported in the literature and are in good agreement with the data obtained[12,13] under experimental conditions most similar to ours: 0.7 mol l^{-1} $NaClO_4$ and 20 °C

$$[\beta_{01} = (4.79, 4.68, 5.08) \cdot 10^3 \text{ and } \beta_{02} = (10.0, 9.77, 6.46) \cdot 10^6].$$

However, the constant β_{03} is somewhat greater than the values reported in the literature[4,6,7,14], $\beta_{03} = (3.98, 3.02, 7.94, 4.68) \cdot 10^8$, which was to be expected, since these were generally determined in nitrate media which, as has been stated in an earlier work[15], are weakly complexing the Cd^{2+} ion, implying that they are not true formation constants, but rather combinations of the stability constants of the simple and mixed coordinated species present in the medium.

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