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Polarography of Lead-Arginine Hydrochloride Complexes

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The complexation of lead ion with arginine hydrochloride has been studied polarographically at 30°C. Four kinds of complex species, $PbCl^+$, $Pb(H_2Arg)Cl^{2+}$, $Pb(H_2Arg)(OH)^{2+}$ and $Pb(H_2Arg)_2(OH)^{3+}$ (where H_2Arg denotes the arginine univalent cation) were confirmed in various pH range, respectively. The logarithmic dissociation constant of $Pb(H_2Arg)_2(OH)^{3+}$ was found to be 10.33 ± 0.03 at ionic strength 0.9.

The complexes of arginine with copper and zinc have been studied by polarographic and other methods and the metal-ligand ratios have been shown to be 1 : 1 and 1 : 2.[1-3] The effect of amino acid structure on the stability of the complexes formed with metals of Hg, Be, Zn and Cd has been reported by Perkins.[4,5] The stability constant of calcium-arginine chelate was determined by pH titration method.[6] The effect of temperature on the dissociation constants of arginine and its different metal complexes was investigated by Pelletier.[7]

This paper presents the results of the polarographic behavior of lead-arginine hydrochloride system.

Experimental

Apparatus. All polarograms were recorded manually using a Sargent Model XII Polarograph, equipped with a Leeds and Northrup Student Potentiometer. A modified H-cell, containing an external saturated calomel reference electrode (SCE) and a potassium chloride - agar plug was used. All experiments were carried out at 30 ± 0.1°C.

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[1] N. C. Li and E. Doody, *J. Am. Chem. Soc.*, **74**, 4184 (1952).

[2] N. C. Li and E. Doody, *ibid.*, **76**, 221 (1954).

[3] A. Taurins, *Can. J. Res.*, **28B**, 762 (1950).

[4] D. J. Perkins, *Biochem. J.*, **51**, 487 (1952).

[5] D. J. Perkins, *ibid.*, **55**, 649 (1953).

[6] M. Hardel, *Z. Physiol. Chem.*, **346**, 224 (1966).

[7] S. Pelletier, *Compt. Rend.*, **248**, 2567 (1959).

The mercury flow rate and the dropping time of the capillary used were 2.067 mg/sec and 3.56 sec respectively at an applied potential −0.5 V *vs.* SCE with the mercury column height 73.2 cm, measured in a solution which contained 1.0 mM lead nitrate, 0.4 M arginine hydrochloride, 0.5 M sodium nitrate, and 0.003% Triton X-100 at pH 6.85.

Chemicals. The stock solution of 0.01 M lead nitrate was prepared and analyzed as described previously.[8] The arginine hydrochloride (Aldrich Chemical Co.) was research grade and the solutions were freshly prepared before use. Triton X-100 was used as a maximum suppressor. Sodium nitrate was used as supporting electrolyte with which the ionic strength of the polarographic solutions were adjusted to 0.9. The pH values of the polarographic solutions were adjusted with nitric acid or sodium hydroxide and no buffer was used.

Results and Discussion

The polarographic characteristics of the lead-arginine hydrochloride complex were studied with the solutions which contained 1.0 mM lead nitrate and varying concentration of arginine hydrochloride from 0.1 M to 0.6 M over the pH range 0.80—9.05. At higher pH value precipitation occurred when the arginine hydrochloride concentration was lower than 0.2 M.

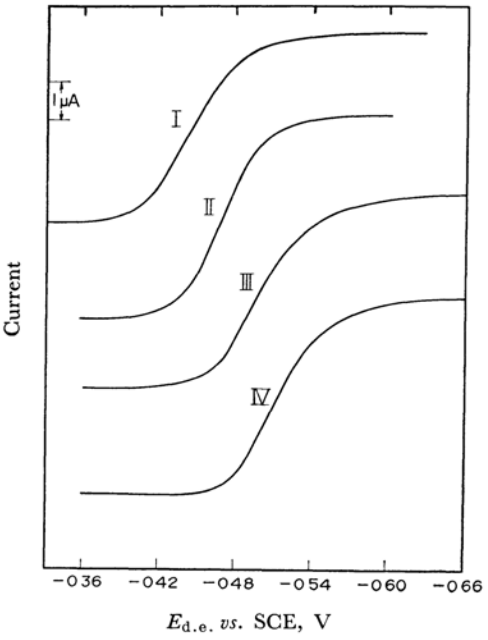

Fig. 1. Polarograms at various conditions.
1.0 mM $Pb(NO_3)_2$, $NaNO_3$ at μ 0.9, $[Cl^-]=C_{\mathrm{Arg}}$
I 0.006% Triton X-100, C_{Arg} 0 M, pH 2.68
II 0.003% Triton X-100, C_{Arg} 0.2 M, pH 7.92
III 0.003% Triton X-100, C_{Arg} 0.2 M, pH 8.62
IV 0.003% Triton X-100, C_{Arg} 0.2 M, pH 9.05

As shown in Table 1 a reversible two-electron reduction was held at pH lower than 8.30 for the ligand concentrations between 0.1 M to 0.4 M and

TABLE 1. EVIDENCE FOR THE REVERSIBILITY
(1.0 mM $Pb(NO_3)_2$, 0.003% Triton X-100 and $NaNO_3$ at μ 0.9)

C_{Arg} (M)	pH	$-E_{1/2}$ *vs.* SCE (V)	$-\Delta E_{\mathrm{d.e.}}/\Delta\log\frac{i}{i_d-i}$
0.1	0.91	0.406	0.030
	1.42	0.408	0.031
	2.62	0.410	0.031
	3.20	0.411	0.031
	4.00	0.412	0.030
	4.95	0.411	0.032
	6.18	0.423	0.029
	6.99	0.430	0.032
	7.47	0.442	0.030
	8.00	0.461	0.031
0.2	0.80	0.408	0.031
	1.45	0.408	0.030
	2.73	0.414	0.029
	4.18	0.415	0.032
	5.00	0.416	0.031
	6.05	0.427	0.028
	7.58	0.450	0.030
	8.00	0.476	0.031
0.4	0.95	0.417	0.029
	2.45	0.426	0.031
	4.50	0.427	0.028
	5.30	0.429	0.031
	6.55	0.442	0.029
	7.23	0.460	0.032
	8.30	0.502	0.030
0.6	1.30	0.423	0.029
	3.10	0.432	0.031
	4.71	0.433	0.030
	6.05	0.443	0.030
	7.78	0.488	0.028
	8.80	0.528	0.030
	8.95	0.531	0.030
	9.05	0.536	0.029

TABLE 2. QUASI-REVERSIBLE CHARACTER ABOVE pH 8.30
(1.0 mM $Pb(NO_3)_2$, 0.003% Triton X-100 and $NaNO_3$ at μ 0.9)

C_{Arg} (M)	pH	$-E_{1/2}$ *vs.* SCE (V)	$-\Delta E_{\mathrm{d.e.}}/\Delta\log\frac{i}{i_d-i}$
0.1	8.05	0.464	0.031
	8.30	0.471	0.039
0.2	8.20	0.483	0.030
	8.45	0.490	0.039
	9.05	0.513	0.038
0.4	8.00	0.491	0.029
	8.80	0.518	0.038
	9.05	0.528	0.039

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[8] T. T. Lai and C. C. Hsieh, *J. Electrochem. Soc.*, **112**, 218 (1965).

at pH lower than 9.05 for the ligand concentration 0.6 M.

At $\text{pH} > 8.30$ and ligand concentrations between 0.1 M and 0.4 M the electrode process was regarded as a quasi-reversible reduction as can be evidenced from the slopes of $\log i/(i_d - i)$ *vs.* $E_{\text{d.e.}}$, 0.038—0.039 (Table 2), and the asymmetrical waves (Fig. 1). The distortion of the polarograms was attributed to the adsorption effect of the maximum suppressor.[9,10] In confirm this assertion solutions containing higher concentration of maximum suppressor were polarographed. As can be observed from the curve 1 in Fig. 1, the addition of 0.006% Triton X-100, was enough to cause the wave become asymmetric when the polarographic solution contained no chelating agent.

The temperature coefficient of the half-wave potential was $-0.2\ \text{mV}/°\text{C}$ at $\text{pH} < 8.30$ and in the conditions of the asymmetrical waves it was $-0.7\ \text{mV}/°\text{C}$, which is still in the limiting value for a reversible reduction.

The constant value of $i_d/\sqrt{h}$, 0.766 ± 0.014, for $h = 71.6$—32.2 cm and ligand concentration 0.1 M at pH 6.18, revealed that the limiting current was entirely diffusion-controlled.

The temperature coefficient of the diffusion current was 1.4%/°C in the whole pH range investigated in this work. This also proves the diffusion-controlled system.

Effect of pH on Half-wave Potential and Diffusion Current. The dependences of half-wave potential and diffusion current on the pH value are shown in Figs. 2 and 3 respectively. In the two figures the curves all break into four sections at the same pH values. This fact reveals the existence of four kinds of complex species at each section of $\text{pH} < 2.0$, pH 2.0—5.0, pH 5.0—7.0 and pH 7.0—9.1.

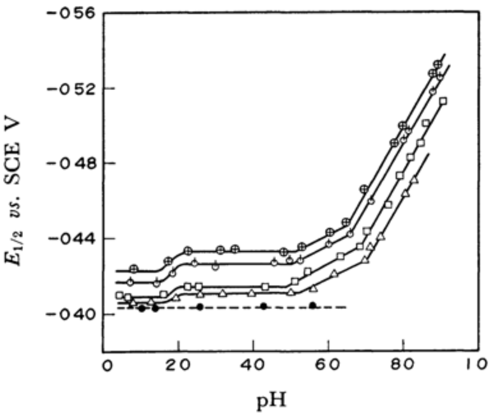

Fig. 2. Variation of half-wave potential with pH. 1.0 mM $Pb(NO_3)_2$, 0.003% Triton X-100, $NaNO_3$ at μ 0.9 $[Cl^-] = C_{\text{Arg}}$

	C_{Arg} (M)
●	0
△	0.1
□	0.2
○	0.4
⊕	0.6

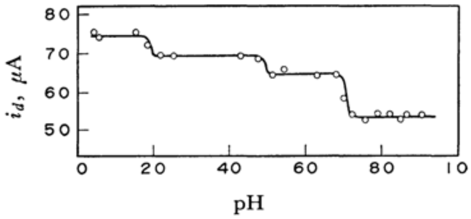

Fig. 3. Effect of pH on the diffusion current. 1.0 mM $Pb(NO_3)_2$, 0.003% Triton X-100, $NaNO_3$ at μ 0.9 $[Cl^-] = C_{\text{Arg}} = 0.2$ M

The horizontal lines at $\text{pH} < 2.0$ for varying concentrations of complexing agent in Fig. 2 were ascribed to the formation of the lead chloro complex rather than the lead-arginine complex, as can be confirmed by the half-wave potential data of the lead-sodium chloride system in Table 3.

In the pH range 2.0—5.0, the half-wave potentials shifted a little to negative side, and the diffusion current decreased (Fig. 3). These changes indicate the participation of arginine ligand to the lead-chloro complex.

In the pH range 5.0—7.0 in Fig. 2, the slope of the curve is 0.010 V. This minute slope demonstrates the partial substitution of the chloride ligand in the lead complex with the hydroxyl ligand and the releasing of the hydroxyl ion in the cathodic reduction. The higher the ligand concentration, the greater the shifting of the breaking point to lower pH value. This fact indicates that the higher arginine concentration is in favor of the substitution of the chloride ligand with the hydroxyl ligand.

When the pH value is greater than 7.0, the $E_{1/2}$ *vs.* pH curves show a third inflection with a slope of 0.034 V, showing that one hydroxyl ion was involved in the reduction.

It is obvious from Fig. 3, that each change in complex species resulted in a separate diffusion current drop.

Effect of Ligand Concentration on Half-wave Potential. To determine the metal-ligand ratio of the lead-arginine hydrochloride complexes, the half-wave potentials were plotted against the logarithm of the concentration of arginine hydrochloride (Fig. 4).

As shown in Fig. 4, lead does not form complexes with arginine hydrochloride below pH 5.0 when the ligand concentration is lower than 0.22 M. At $\text{pH} < 2.0$ and $C_{\text{Arg}} > 0.22$ M, the reciprocal slope is 0.030 V. In referring to the Fig. 2 and Table 3, the formation of the complex species, $PbCl^+$, was

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[9] J. Koryta, *Coll. Czech. Chem. Commun.*, **18**, 206 (1953).

[10] J. Weber, J. Koutecky and J. Koryta, *Z. Electrochem.*, **63**, 583 (1959).

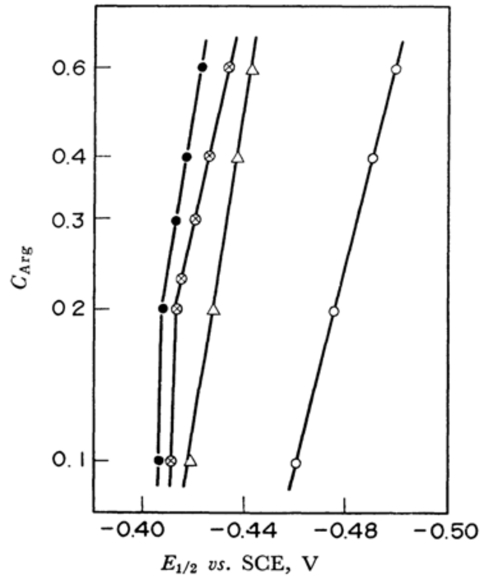

Fig. 4. Plots of C_{Arg} vs. $E_{1/2}$ ($[Cl^-]=C_{Arg}$). 1.0 mM $Pb(NO_3)_2$, 0.003% Triton X-100, $NaNO_3$ at μ 0.9
● pH 1.08; ⊗ pH 3.00; △ pH 6.05; ○ pH 8.00

proved. When $C_{Arg}>0.22$ M, the reciprocal slopes of the other curves in Fig. 4 are 0.044 V, 0.030 V, and 0.050 V; those values show the ligand numbers to be 1.5, 1.0 and 1.7 for the pH ranges 2.0—5.0, 5.0—7.0 and 7.0—9.1 respectively.

TABLE 3. POLAROGRAPHIC CHARACTERISTICS OF Pb-NaCl SYSTEM AT LOW pH REGION (1.0 mM $Pb(NO_3)_2$, 0.003% Triton X-100 and $NaNO_3$ at μ 0.9)

NaCl (M)	pH	$-E_{1/2}$ vs. SCE (V)	i_d (μA)	$-\Delta E_{d.e} \Big/ \Delta \log \frac{i}{i_d-i}$
0.1	0.78	0.407	7.75	0.030
	3.08	0.406	7.54	0.031
0.2	0.69	0.409	7.85	0.031
	1.40	0.408	7.65	0.030
	3.00	0.409	7.65	0.030
0.4	1.34	0.417	7.60	0.032
	2.71	0.417	7.70	0.031
	2.58	0.417	7.80	0.029
	3.50	0.417	7.70	0.030
0.6	2.55	0.423	7.60	0.031
	3.81	0.423	7.70	0.029

The competition between arginine and chloride ion for electron pair donation to the lead ion was demonstrated in Fig. 5, in which the polarographic solutions contained sodium chloride besides arginine hydrochloride to maintain the chloride ion concentration at 0.60 M.

It is evident from Fig. 5, when $C_{Arg}<0.22$ M and $[Cl^-]=0.60$ M, the chloride ion predominate arginine in the competition for electron pair donation in the pH range 2.0—9.1. Even under the condition, $C_{Arg}>0.22$ M at pH<5.0, the arginine ligand predominates scarcely the chloride ligand, and the arginine coordinates with lead ion rather weakly, as can be confirmed from the minute reciprocal slope 0.016 V in Fig. 5. When $C_{Arg}>0.22$ M, the reciprocal solopes are 0.030 V and 0.052 V for the pH ranges 5.0—7.0 and 7.0—9.1, respectively, indicating the formation of 1 : 1 and 1 : 2 lead-arginine complexes in these pH ranges.

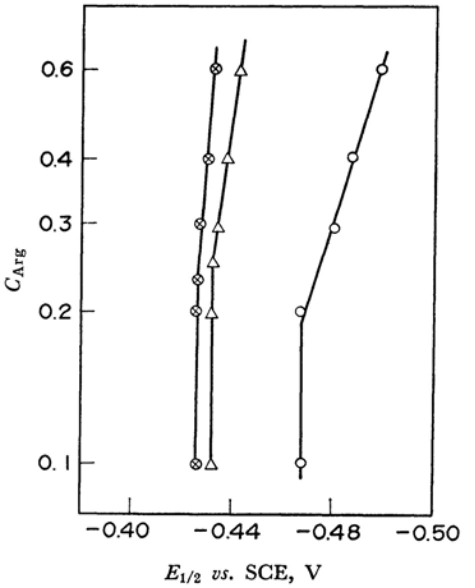

Fig. 5. Plots of log C_{Arg} vs. $E_{1/2}$ ($[Cl^-]=0.60$ M). 1.0 mM $Pb(NO_3)_2$, 0.003% Triton X-100, $NaNO_3$ at μ 0.9
⊗ pH 3.00; △ pH 6.05; ○ pH 8.00

Complex Species and Dissociation Constant. The pK_1 and pK_2 values of arginine are 2.17 and 9.04[11] and the isoelectric point is 10.76,[12] so that the predominant ligand species in the pH region studied in this work must be arginine univalent cation (H_2Arg^+) rather than the dipclar molecule (HArg).

If a complex $Pb(H_2Arg)_m(OH)_nCl_r^{2+m-n-r}$ was formed in the solution, the cathodic reduction at the dropping mercury electrode must be

$$Pb(H_2Arg)_m(OH)_nCl_r^{2+m-n-r} + 2e + Hg$$
$$= Pb(Hg) + mH_2Arg^+ + nOH^- + rCl^- \quad (1)$$

The shift of the half-wave potential by complexation and reduction in Eq. (1) must obey:

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[11] E. H. Rodd, "Chemistry of Carbon Compounds," Vol. 1, Elsevier Publishing Co. (1951), p. 1341.

[12] L. F. Fieser and M. Fieser, "Introduction to Organic Chemistry," D. C. Heath and Co., Boston (1957), p. 301.

TABLE 4. LIGAND NUMBER AND COMPLEX SPECIES

pH range	Ligand concn. $C_{Arg}=[Cl^-]$	Total ligand No. $(m+r)$	Arginine ligand No. (m)	Cl^- ligand No. (r)	OH^- ligand No. (n)	Complex species
0.8—2.0	0—0.22	0	0	0	0	Pb^{2+}
	0.22—0.6	1.0	0	1.0	0	$PbCl^+$
2.0—5.0	0—0.22	0	0	0	0	Pb^{2+}
	0.22—0.6	1.5	0.5	1.0	0	$Pb(H_2Arg)Cl^{2+}$
5.0—7.0	0.22—0.6	1.0	1.0	0	0.3	$Pb(H_2Arg)(OH)^{2+}$
7.0—9.1	0.22—0.6	1.7	1.7	0	1.1	$Pb(H_2Arg)_2(OH)^{3+}$

$$(E_{1/2})_c = (E_{1/2})_s + 0.030\log K_c - 0.030\log(D_c/D_s) - 0.030m\log[H_2Arg^+] - 0.030n\log[OH^-] - 0.030r\log[Cl^-] \quad (2)$$

where $K_c = \dfrac{[H_2Arg^+]^m[OH^-]^n[Cl^-]^r[Pb^{2+}]}{[Pb(H_2Arg)_m(OH)_nCl_r{}^{2+m-n-r}]}$

D_c and D_s are diffusion coefficients of complex and simple lead ion, respectively.

For $pK_1 < pH < pK_2$

$$C_{Arg} \simeq [H_2Arg^+] = [Cl^-]$$

and $-\log[OH^-] = 14 - pH$

where C_{Arg} is the nominal concentration of arginine hydrochloride solution, then, the values of m, n and r can be determined as follows:

$m + r = -\Delta(E_{1/2})_c/0.030(\Delta\log C_{Arg})$ (when pH keeps constant)

$m = -\Delta(E_{1/2})_c/0.030(\Delta\log C_{Arg})$ (when both pH and $[Cl^-]$ keeps constant)

$n = -\Delta(E_{1/2})_c/0.030(\Delta pH)$ (when C_{Arg} keeps constant)

and $r = (m + r) - m$

Results based on the foregoing polarographic data and discussion were summarized in Table 4. Thus, the predominant complex species formed in various pH range were proved to be $PbCl^+$, $Pb(H_2Arg)Cl^{2+}$, $Pb(H_2Arg)(OH)^{2+}$ and $Pb(H_2Arg)_2(OH)^{3+}$ for pH <2.0, pH 2.0—5.0, pH 5.0—7.0 and pH 7.0—9.1, respectively. These change in complex species and the increment in the size for each complex may cause the stepwise decrease in diffusion current. This reduction was in good agreement with the results in Fig. 3 and was supported by Fig. 2.

Although from the data in Figs. 2, 4 and 5 the assignment of other formula $Pb(H_2Arg)(Harg)^{3+}$ in pH 7.0—9.1 is possible, the calculated dissociation constant (pK_c=4.87±0.03) (Table 5) shows that it is much less stable than $Pb(H_2Arg)_2(OH)^{3+}$ (pK_c=10.33+0.03) (Table 6), so that the latter formula was adopted as a predominant species.

TABLE 5. DISSOCIATION CONSTANTS OF $Pb(H_2Arg)(HArg)^{3+}$

pH	C_{Arg}	$(E_{1/2})_s-(E_{1/2})_c$	$(i_d)_c/(i_d)_s$	pK_c
7.0	0.1	0.026	0.79	4.87
	0.2	0.040	0.73	4.84
	0.4	0.056	0.72	4.87
	0.6	0.065	0.71	4.88
8.0	0.1	0.057	0.73	4.87
	0.2	0.072	0.71	4.87
	0.4	0.087	0.67	4.87
	0.6	0.096	0.64	4.88
				ave. 4.87±0.03

TABLE 6. DISSOCIATION CONSTANT OF $Pb(H_2Arg)_2(OH)^{3+}$

pH	C_{Arg}	$(E_{1/2})_s-(E_{1/2})_c$	$(i_d)_c/(i_d)_s$	pK_c
7.0	0.1	0.026	0.79	10.33
	0.2	0.040	0.73	10.30
	0.4	0.056	0.72	10.34
	0.6	0.065	0.71	10.35
8.0	0.1	0.057	0.73	10.33
	0.2	0.072	0.71	10.33
	0.4	0.087	0.67	10.33
	0.6	0.096	0.64	10.34
				ave. 10.33±0.03

In these complex species mentioned above only the complex species $Pb(H_2Arg)_2(OH)^{3+}$ in pH 7.0—9.1 can be regarded as a steady form and the others are in transition.

When a complex species $Pb(H_2Arg)_m(OH)_n{}^{2+m-n}$ is reduced reversibly, the half-wave potential obeys the Eq. (2) except losing the last term, $-0.030\,r\log[Cl^-]$.

In pH range, $pK_1 \ll pH < pK_2$

$$[H_2Arg^+] = \frac{C_{Arg}\cdot[H^+]}{[H^+]+K_2}$$

and $D_c/D_s = (i_d)_c/(i_d)_s$

$$\text{then, } pK_c = \frac{(E_{1/2})_s-(E_{1/2})_c}{0.030} - \frac{1}{2}\log(i_d)_c/(i_d)_s - m\log C_{Arg} + (m-n)pH + m\log([H^+]+K_2) + 14n$$

It has been shown above that at pH 7.0—9.1, $m=1.7$ (Fig. 4) and $n=1.1$ (Fig. 2). Then, the dissociation constant of the comlpex $Pb(H_2Arg)_2(OH)^{3+}$ was calculated to be $pK_c=10.33+0.03$ (Table 6).

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