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Polarography of Pb(II) Complexes with *N*,*N*′-Bis(2-hydroxyethyl)ethylenediamine-*N*,*N*′-diacetic Acid

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Synopsis. The electrochemical behaviour of the Pb(II)-*N*,*N*′-Bis(2-hydroxyethyl)ethylenediamine-*N*,*N*′-diacetic acid(H_2bhedda$=H_2L$) system has been examined by means of d.c. polarography. Two well-defined polarographic reduction waves were observed. The mechanisms of the electrode reaction for the two waves were elucidated. The kinetic parameters of the irreversible reduction of the complexes have been evaluated; $k_{f1}=3.80\times10^{-5}$ cm/s and $k_{f2}=5.25\times10^{-16}$ cm/s. The stability constant of the $PbHL^+$ species is calculated to be $10^{1.45}$.

Many workers[1,2)] have reported on the electrochemical behaviour of H_4edta derivative complexes with several kinds of metals. We ourselves have previously studied the mechanisms of the electrode reactions of Pb(II)-H_6ttha(triethylenetetramine-*N*,*N*,*N*′,*N*″,*N*‴,*N*‴-hexaacetic acid) and Cd(II)-H_2bhedda(*N*,*N*′-bis-(2-hydroxyethyl)ethylenediamine-*N*,*N*′-diacetic acid) complexes.[3-5)] Little is known, however, concerning the properties of the H_2bhedda ligand and its metal complexes, except for the acid-dissociation constants.[6)] In this report, the mechanisms and parameters of the electrode reactions for Pb(II)-H_2bhedda complexes are investigated. The influence of the hydroxymethyl groups on the stability constant and the rate constant of the reduction is also discussed.

Experimental

A Pb(II) solution(Pb(II) aquo ion) was prepared by dissolving reagent-grade lead nitrate. The ligand, H_2bhedda (Clewat OH-300, Teikoku Chemical Co.) was twice recrystallized from hot water, and 0.01 mol dm^{-3} solution was prepared. The acetate buffer solutions were used to adjust the pH values of the test solutions. A sodium perchlorate solution (1.0 mol dm^{-3}) was added to keep the ionic strength constant ($\mu=0.4$).

Results and Discussion

Polarograms of Pb(II)-H_2bhedda System. The polarogram of the Pb(II)-H_2bhedda system exhibited a maximum(−0.84 V *vs.* SCE). Triton X-100 (up to 1.7×10^{-4}%) was added to suppress the maximum. In an excess of the metal ion to the ligand, the polarograms gave two well-defined reduction waves(Fig. 1). The two waves are referred to as Wave A (first wave) and Wave B(second wave). In an excess of the ligand, the limiting current for Wave A was independent of the mercury-head height below pH 4.0. The temperature coefficient of the limiting current for Wave A was 3.5% (pH=3.28, M:L=1:5). From the analysis of *i*-*t*(*i*:current, *t*:time) curves for Wave A, the value of γ in the equation, $i=kt^{\gamma}$, was calculated to be 0.67(pH=3.28, 1:5, −0.7 V *vs.* SCE). The limiting current for Wave A involves a kinetic characteristic below pH 4.0 in an excess of the ligand.

As the limiting current for Wave B was proportional to the square root of the mercury-head height at any pH, and the temperature coefficient of the limiting current for Wave B was 1.5%(1:5, pH=4.9), the limiting current for Wave B can safely be said to be diffusion-controlled. The average value of the reciprocal slope of the conventional log-plot for Wave B was 47.1 mV, and so Wave B is considered to be an irreversible two-electron reduction wave.

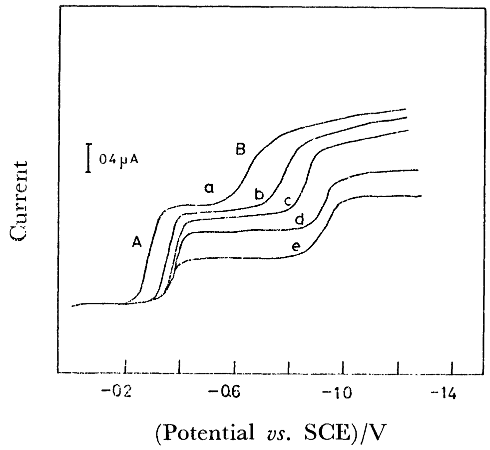

Fig. 1. Polarograms of Pb(II)-H_2bhedda system varying with pH.
$[Pb]_t=5.0\times10^{-4}$ mol dm^{-3}, $[H_2bhedda]_t=2.5\times10^{-4}$ mol dm^{-3}, $\mu=0.4(NaClO_4)$, acetate buffer, pH —— (a) 3.05, (b) 3.53, (c) 4.08, (d) 5.19, (e) 7.72. A: Wave A, B: Wave B.

Test of Kinetic Current Theory for Wave A. The rate-determining step of the kinetic process for Wave A in an acetate buffer is expressed as follows;

$$PbHL^+ + qH^+ \xrightarrow{k_d} Pb^{2+} + H_{q+1}L, \tag{1}$$

$$Pb^{2+} + jOAc^- \rightleftharpoons Pb(OAc)_j^{2-j}. \tag{2}$$

The following relationship, derived by Koryta,[7)] is applicable to such a kinetic current;

$$\left(\frac{(i_k)_a}{(i_d)_a-(i_k)_a}\right)\left(1+\frac{(i_k)_a}{(i_d)_a}\cdot\frac{C_M}{C_L}\cdot\frac{K_{PbHL}\cdot\delta_{HL}/\sum_{p=0}^{1}K_{PbHL_p}\cdot\delta_{H_pL}}{\delta_{H(q+1)L}}\right)^{1/2}$$
$$=0.886[H^+]^q\sqrt{\frac{k_d\cdot t_d\sum_{j=0}^{p}(K_0'\cdots K_j'[OAc]^j)}{K_{eq}\cdot C_L\cdot\delta_{H(q+1)L}}}, \tag{3}$$

where C_M is the total concentration of Pb(II); δ_{H_pL}, the molar distribution ratio of H_pL species; q, the number of the proton participating in reaction (1); k_d, the dissociation rate constant of the complex; t_d, the dropping time; [OAc], the concentration of the acetate ion, and $K_{eq}=[PbHL][H^+]^q/[Pb^{2+}][H_{(q+1)}L]$. The effect of the acetate buffer solution on the kinetic current $(i_k)_a$ was also considered. The value of $\sum(K_0'\cdots K_j'[OAc]^j)$ was obtained from the shift of the half-wave potential. The plot of

$$F_1=\log\frac{(i_k)_a}{(i_d)_a-(i_k)_a}$$
$$+\frac{1}{2}\log\left(1+\frac{(i_k)_a}{(i_d)_a}\cdot\frac{C_M}{C_L}\cdot\frac{K_{PbHL}\cdot\delta_{HL}/\sum_{p=0}^{1}K_{PbH_pL}\cdot\delta_{H_pL}}{\delta_{H(q+1)L}}\right)vs.$$
]

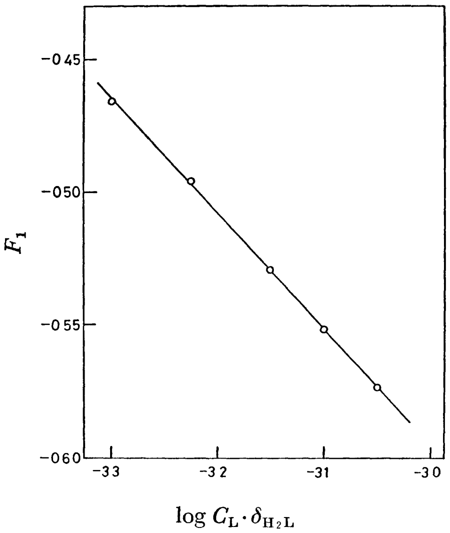

Fig. 2. Test of kinetic current theory for Wave A (Plot of F_1 *vs.* $\log C_L \cdot \delta_{H_2L}$)

$$\left(F_1 = \log \frac{(i_k)_a}{(i_d)_a - (i_k)_a} + \frac{1}{2} \times \log\left(1 + \frac{(i_k)_a}{(i_d)_a} \cdot \frac{C_M}{C_L} \cdot \frac{K_{PbHL} \cdot \delta_{HL} / \sum_{p=0}^{1} K_{PbH_pL} \cdot \delta_{H_pL}}{\delta_{H(q+1)L}}\right)\right)$$

$[Pb]_t = 5.0 \times 10^{-4}$ mol dm^{-3}, $[H_2bhedda]_t = 5.0 \times 10^{-4}$, -9.0×10^{-4} mol dm^{-3}, $\mu = 0.4(NaClO_4)$, acetate buffer

$\log C_L \cdot \delta_{H_2L}$ is shown in Fig. 2. The slope of the straight line (−0.43) is consistent with the theoretical value of Eq. 3 (−0.5). Thus, the number of the proton participating in the above reaction mechanism could be obtained by plotting F_1 *vs.* pH ($q=1$). The average dissociation rate constant(k_d) of the complex was also calculated($k_d = 1.49 \pm 0.43$ s^{-1}, pH=2.95—3.53).

Electrode Reaction for Wave B. The dependence of the half-wave potential $(E^{irr}_{1/2})_b$ on the pH was remarkably changed from −92 mV/pH to −4.0 mV/pH at pH 5.4. In order to analyze the irreversible reduction mechanisms for Wave B, a theoretical equation proposed by Vlček,[3)] could be used. By assuming that the complex species, PbL, participates in the reaction in the pH range from 4.0 to 5.4, the number of the proton is found to be 2. The electrode reaction mechanism is expressed as follows:

$$PbL + 2H^+ + 2e + Hg \xrightarrow[k_{j_1}]{} Pb(Hg) + H_2L. \qquad (4)$$

The electrode reaction rate constant, k_{j_1}, was calculated ($k_{j_1} = 3.80 \times 10^{-5}$ cm/s at $E^{irr}_{1/2} = -0.888$ V *vs.* SCE). Above pH 5.4, the mechanism of the electrode reaction can also be expressed as follows:

$$PbL + 2e + Hg \xrightarrow[k_{j_2}]{} Pb(Hg) + L^{2-}, \qquad (5)$$

where k_{j_2} was calculated to be 5.25×10^{-16} cm/s($E^{irr}_{1/2} = -0.947$ V *vs.* SCE).

The stability constants[7),8)] of the Pb(II)–H_2bhedda and Pb(II) complexes with the analogous H_2bhedda ligands are shown in Table 1. Both of the stability constants, K_{PbL} and K_{PbHL}, become smaller in the order of the ligands: H_4edta>H_3hedta>H_2bhedda. This results from the drop in the coordinating ability of the ligand due to the substitution of the hydroxymethyl group for the carboxyl group in the ligand. The small value of k_{j_2} (pH>5.4) for H_2bhedda results from the increase on the transfer coefficient, the negative shift of the half-wave potential, and the steric hindrance caused by uncoordinated hydoxymethyl groups in H_2bhedda.

TABLE 1. LOGARITHMIC STABILITY CONSTANTS AND KINETIC PARAMETERS

(1) Stability constants

	PbL	PbHL	Ref.
H_4edta	18.04	10.61	7
H_3hedta	14.85	7.68	8
H_2bhedda	11.1	4.45	Authors

(2) Kinetic parameters

	α		$(-E^0_p$ *vs.* SCE)/V		k_j/cm s^{-1}		
	(PbHL)	(PbL)	(PbHL)	(PbL)	(PbHL)	(PbL)	Ref.
H_4edta	0.26	0.26	0.718	—	8.7×10^{-6}	1.2×10^{-6}	2
H_3hedta	0.36	0.36	0.618	—	2.4×10^{-4}	7.9×10^{-5}	2
H_2bhedda	—	0.63	—	0.715[a)]	a kinetic nature	$3.8 \times 10^{-5} (k_{j_1})$ $(4.0 < pH \leqq 5.4)$ $5.25 \times 10^{-16} (k_{j_2})$ $(pH > 5.4)$	Authors

α: Transfer coefficient, k_j: formal electrode-reaction rate constant.

a) $E^0_p = -0.388 - 0.0295 \log (\beta_{101}/\beta_{001})$ ($\beta_{101} = K_{PbL}$, $\beta_{001} = 1$).

TABLE 2. DISSOCIATION RATE CONSTANTS (pH=3.2)

	k_d/s^{-1}	Ref.
$Pbhedta^- + H^+ \rightarrow Pb^{2+} + Hhedta^{2-}$	47.6	9
$Pbedta^{2-} + H^+ \rightarrow Pb^{2+} + Hedta^{3-}$	0.442	9
$Pbcydta^{2-} + H^+ \rightarrow Pb^{2+} + Hcydta^{3-}$	2.52×10^{-4}	9
$Pbdtpa^{3-} + H^+ \rightarrow Pb^{2+} + Hdtpa^{4-}$	0.183	9
$PbHbhedda^+ + H^+ \rightarrow Pb^{2+} + H_2bhedda$	1.5	Authors

H_3hedta: *N*-(2-Hydroxyethyl)ethylenediamine-*N,N′,N′*-triacetic acid. H_4edta: Ethylenediamine-*N,N,N′,N′*-tetraacetic acid. H_4cydta: *trans*-1,2-Cyclohexylenedinitrilotetraacetic acid. H_5dtpa: Diethylenetriamine-*N,N,N′,N″,N″*-pentaacetic acid.

Some dissociation-rate constants[9)] for Pb(II) complexes with H_3hedta, H_4edta, H_4cydta, H_5dtpa, and H_2bhedda are shown in Table 2. All these dissociation-rate constants except for that of H_2bhedda correspond to the dissociation of the unprotonated Pb(II) complex participating with each proton. The result for the Pb(II)–H_2bhedda complex indicates that the reaction scheme differs from the other complexes given in Table 2.

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