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A Polarographic Study of the Complex Formation Equilibria of the Lead(II) Ion with Aspartic and Iminodiacetic Acids

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In this experiment, we studied the complex formation equilibria of the lead(II) ion with aspartic acid and iminodiacetic acid by using the polarographic method. In acetate buffer solutions ($5.80 > \mathrm{pH} > 3.70$), the lead(II) ion forms one normal complex, PbX^0, and two mixed ligand complexes involving the acetate ion, $PbX(Ac)^-$ and $PbX(Ac)_2{}^{2-}$, with aspartic acid. On the other hand, with iminodiacetic acid, it forms a normal complex, PbX^0, and only one mixed ligand complex, $PbX(Ac)^-$. By observing the effects of the concentrations of the hydrogen ion, the acetate ion, and aspartic acid or iminodiacetic acid on the half-wave potential of the lead(II) ion, their formation constants were determined to be as follows:

$$(K^{\mathrm{Ac}}_{\mathrm{PbX}})_{\mathrm{Asp}} = \frac{[\mathrm{PbX(Ac)^-}]}{[\mathrm{PbX^0}]\cdot[\mathrm{Ac^-}]} = 7.0\times 10, \quad (K^{\mathrm{Ac}}_{\mathrm{PbX(Ac)}})_{\mathrm{Asp}} = \frac{[\mathrm{PbX(Ac)_2{}^{2-}}]}{[\mathrm{PbX(Ac)^-}]\cdot[\mathrm{Ac^-}]} = 1.3_4,$$

$$(K^{\mathrm{Ac}}_{\mathrm{PbX}})_{\mathrm{IDA}} = \frac{[\mathrm{PbX(Ac)^-}]}{[\mathrm{PbX^0}]\cdot[\mathrm{Ac^-}]} = 3.0, \quad (K_{\mathrm{PbX}})_{\mathrm{Asp}} = \frac{[\mathrm{PbX^0}]}{[\mathrm{Pb^{2+}}]\cdot[\mathrm{X^{2-}}]} = 1.0_6\times 10^6,$$

$$(K_{\mathrm{PbX}})_{\mathrm{IDA}} = \frac{[\mathrm{PbX^0}]}{[\mathrm{Pb^{2+}}]\cdot[\mathrm{X^{2-}}]} = 5.7_0\times 10^7, \quad (K^{\mathrm{X}}_{\mathrm{PbX}})_{\mathrm{Asp}} = \frac{[\mathrm{PbX_2{}^{2-}}]}{[\mathrm{PbX^0}]\cdot[\mathrm{X^{2-}}]} = 1.4_2\times 10^2,$$

$$(K^{\mathrm{X}}_{\mathrm{PbX}})_{\mathrm{IDA}} = \frac{[\mathrm{PbX_2{}^{2-}}]}{[\mathrm{PbX^0}]\cdot[\mathrm{X^{2-}}]} = 6.0_6\times 10^3$$

In a previous paper,1) we systematically studied the polarographic behavior of the cadmium(II) ion in an aspartate solution and reported that the cadmium(II) ion can form 1-to-2 as well as 1-to-1 complexes with aspartic acid (Asp). The lead(II) ion can also be expected to form stable complexes with aspartic acid and iminodiacetic acid (IDA). However, few equilibrium studies of the complex formation reaction of the lead(II) ion with these ligand have been conducted. In this connection, it seemed that it would be worthwhile to determine the equilibria between the lead(II) ion and Asp or IDA. In this paper, we will try to determine the solution equilibria between the lead(II) ion and Asp or IDA.

Experimental

Reagents. A standard lead(II) nitrate solution was prepared by dissolving a known amount of pure lead(II) nitrate in redistilled water. Aspartic acid and iminodiacetic acid were recrystallized twice from their aqueous solutions by adding a suitable amount of pure ethanol. The other reagents were of an analytical-reagent grade and were used without further purification. The ionic strength of the sample solution was adjusted by adding an appropriate amount of sodium perchlorate.

Apparatus and Experimental Procedures. All the polarographic studies were conducted in solutions with an ionic strength of 0.30 at 25°C. The DC current-voltage curves were measured by using a manual polarograph similar to that of Kolthoff and Lingane;2) they were corrected for the residual current and the ohmic drop of the cell circuit. In the pH range from 3.70 to 5.80, an acetate buffer was used to keep the solution's pH constant. In an alkaline medium ($8.30 < \mathrm{pH} < 10.40$), however, no buffer reagent was used, because the sample solution always contains an excess amount of uncomplexed Asp or IDA over the lead(II) ion, hence, it is considered to have a buffer capacity sufficient to keep the solution's pH constant.

Results and Discussion

The lead(II) ion in both Asp and IDA solutions invariably gave a single well-defined wave. As is illustrated by the straight lines in Fig. 1, the plot of $\log(i/(i_l - i))$ against the DC potential, E, gave a straight line with a slope falling in the range from -30 to -32 mV, a line corresponding to the two-electron reversible reduction. Here, i_l and i are the limiting current and the current at E respectively. The limiting current was exactly proportional to the bulk concentration of the lead(II) ion and to the square root of the effective pressure on the dropping mercury electrode (these results are not shown here). Therefore, the electrode reaction is reversible in the usual polarographic sense; hence, the half-wave potentials obtained can be analyzed with the aid of the theoretical relation derived thermodynamically.

In an acid solution, when the other experimental conditions are kept constant, the half-wave potential was shifted to more negative potentials by increasing the concentration of Asp or IDA. It was also shifted to the negative potentials by increasing the acetate-ion concentration. From the thermodynamic point of view, the above findings can be interpreted as resulting from the formation of lead(II) complexes of the acetate ion and Asp or the IDA anion. In a usual complex formation reaction, the coordination number of the lead(II) ion is four or six, and IDA and Asp act as tridentate

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1) M. Shibata, H. Mitsuta, M. Inada, and M. Kodama, *Nippon Kagaku Zasshi*, **85**, 767 (1964).

2) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, Interscience Publishers, New York (1952), p. 297.

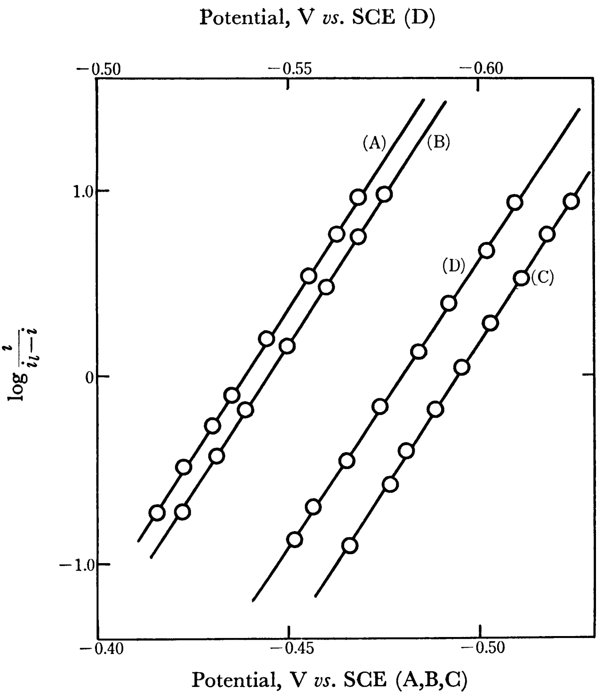
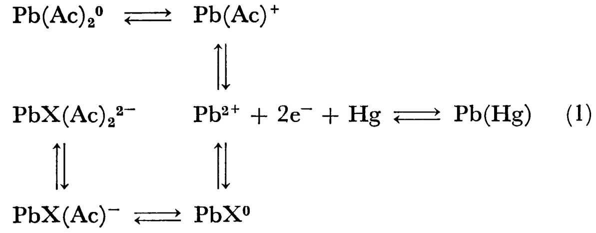


Fig. 1. The plot of log (i/i_l-i) against the *d.c.* potential.
A : Concentration of acetate ion=0.20M
Concentration of lead(II) ion=0.50mM, μ=0.30
Concentration of Asp=70.0 mM, pH=5.62
B : Concentration of acetate ion=0.10M
Concentration of lead(II) ion=0.50mM, μ=0.30
Concentration of IDA=40.0 mM, pH=5.62
C : Concentration of lead(II) ion=0.50 mM
Concentration of Asp=70.0mM, pH=9.33, μ=0.30
D : Concentration of lead(II) ion=0.50 mM
Concentration of IDA=60.0mM, pH=9.50, μ=0.30

ligands. Therefore, as was discussed in connection with the polarography of the copper(II)-GEDTA complex,[3] we can assume the following electrode reaction mechanism for the lead(II) ion in acetate buffer solutions containing Asp or IDA:



$$\begin{array}{lcl}
 & & \mathrm{Pb(Ac)_2^0} \rightleftharpoons \mathrm{Pb(Ac)^+} \\
 & & \qquad\qquad\quad \updownarrow \\
\mathrm{PbX(Ac)_2^{2-}} & & \qquad\qquad\quad \mathrm{Pb^{2+} + 2e^- + Hg \rightleftharpoons Pb(Hg)} \qquad (1) \\
\quad\updownarrow & & \qquad\qquad\quad \updownarrow \\
\mathrm{PbX(Ac)^-} & \rightleftharpoons & \mathrm{PbX^0}
\end{array}$$

with the shift of the half-wave potential corresponding to:

$$\Delta E_{1/2} = 0.0296\left[\log\left(1+\frac{K_{\mathrm{PbAc}}\cdot[\mathrm{Ac}]_f}{(\alpha_H)_{Ac}}+\frac{K_{\mathrm{PbAc}}\cdot K^{\mathrm{Ac}}_{\mathrm{PbAc}}\cdot[\mathrm{Ac}]_f^2}{(\alpha_H)^2_{Ac}} + \frac{K_{\mathrm{PbX}}[\mathrm{X}]_f}{(\alpha_H)_X}+\frac{K_{\mathrm{PbX}}K^{\mathrm{Ac}}_{\mathrm{PbX}}[\mathrm{X}]_f\cdot[\mathrm{Ac}]_f}{(\alpha_H)_X(\alpha_H)_{Ac}} + \frac{K_{\mathrm{PbX}}K^{\mathrm{Ac}}_{\mathrm{PbX}}K^{\mathrm{Ac}}_{\mathrm{PbX(Ac)}}\cdot[\mathrm{X}]_f[\mathrm{Ac}]_f^2}{(\alpha_H)_X(\alpha_H)^2_{Ac}}\right)+\log\frac{k_{\mathrm{PbX}}}{k_{\mathrm{Pb}^{2+}}}\right] \quad (2)$$

where $\mathrm{Ac^-}$ denotes an acetate ion, where $\mathrm{X^{2-}}$ denotes Asp or an IDA bivalent anion, where the k's mean the diffusion current constants, and where $[\mathrm{X}]_f$ and $[\mathrm{Ac}]_f$ are the concentrations of uncomplexed Asp or IDA and of acetic acid respectively. The symbols in Eq. (2) have the following meanings:

$$K_{\mathrm{PbAc}} = \frac{[\mathrm{PbAc^+}]}{[\mathrm{Pb^{2+}}]\cdot[\mathrm{Ac^-}]},\quad K^{\mathrm{Ac}}_{\mathrm{PbAc}} = \frac{[\mathrm{Pb(Ac)_2^0}]}{[\mathrm{PbAc^+}]\cdot[\mathrm{Ac^-}]},$$

$$K_{\mathrm{PbX}} = \frac{[\mathrm{PbX^0}]}{[\mathrm{Pb^{2+}}]\cdot[\mathrm{X^{2-}}]},\quad K^{\mathrm{Ac}}_{\mathrm{PbX}} = \frac{[\mathrm{PbX(Ac)^-}]}{[\mathrm{PbX^0}]\cdot[\mathrm{Ac^-}]},$$

$$K^{\mathrm{Ac}}_{\mathrm{PbX(Ac)}} = \frac{[\mathrm{PbX(Ac)_2^{2-}}]}{[\mathrm{PbX(Ac)^-}]\cdot[\mathrm{Ac^-}]},$$

$$(\alpha_H)_{\mathrm{Ac}} = 1 + [\mathrm{H^+}]/K_a \text{ (acetic acid)},$$

$$(\alpha_H)_{\mathrm{X}} = 1 + [\mathrm{H^+}]/K_2 + [\mathrm{H^+}]^2/K_1\cdot K_2 \text{ (Asp or IDA)}.$$

Since all the polarographic measurements were conducted in solutions containing large excesses of acetic acid and Asp or IDA over the lead(II) ion, the $[\mathrm{X}]_f$ and $[\mathrm{Ac}]_f$ in Eq. (2) can be equated with the total concentrations of acetic acid and Asp or IDA respectively. When the acetate-ion concentration and the solution's pH are kept constant, the plot of the antilog-$(\Delta E_{1/2}/0.0296+\log(k_{\mathrm{Pb}^{2+}}/k_{\mathrm{PbX}}))$ value against $[\mathrm{X}]_f$ invariably gives a linear relation (Fig. 2). This clearly

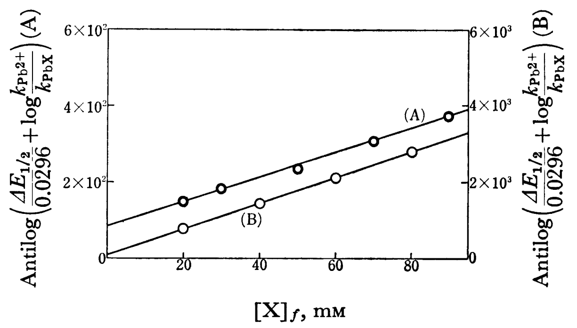


Fig. 2. The plot of antilog$(\Delta E_{1/2}/0.0296 + \log(k_{\mathrm{Pb}^{2+}}/k_{\mathrm{PbX}}))$ against the concentration of uncomplexed Asp or IDA.
A : Asp system
Concentration of acetate ion=0.15M, pH=5.62
Concentration of lead(II) ion=0.50mM, μ=0.30
B : IDA system
Concentration of acetate ion=0.15M, pH=5.62
Concentration of lead(II) ion=0.50mM, μ=0.30

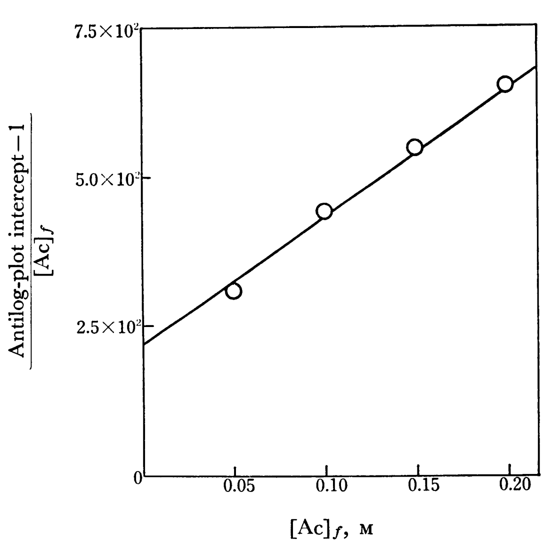


Fig. 3. The plot of (antilog-plot intercept$-1)/[\mathrm{Ac}]_f$ against the concentration of acetate ion.
Asp system:
Concentration of lead(II) ion=0.50mM, μ=0.30, pH=5.62

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[3] M. Kodama and Y. Tominaga, This Bulletin, **42**, 394 (1969).

Table 1. Equilibrium constants (μ=0.30, 25°C)

$$K_{\mathrm{PbAc}}=\frac{[\mathrm{PbAc}^+]}{[\mathrm{Pb}^{2+}]\cdot[\mathrm{Ac}^-]}=2.1_8\times10^2$$

$$K^{\mathrm{Ac}}_{\mathrm{PbAc}}=\frac{[\mathrm{Pb(Ac)_2}^0]}{[\mathrm{PbAc}^+]\cdot[\mathrm{Ac}^-]}=9.7_0$$

$$(K_{\mathrm{PbX}})_{\mathrm{Asp}}=\frac{[\mathrm{PbX}^0]}{[\mathrm{Pb}^{2+}]\cdot[\mathrm{X}^{2-}]}=1.0_6\times10^6$$

$$(K_{\mathrm{PbX}})_{\mathrm{IDA}}=\frac{[\mathrm{PbX}^0]}{[\mathrm{Pb}^{2+}]\cdot[\mathrm{X}^{2-}]}=5.7_0\times10^7$$

$$(K^{\mathrm{X}}_{\mathrm{PbX}})_{\mathrm{Asp}}=\frac{[\mathrm{PbX_2}^{2-}]}{[\mathrm{PbX}^0]\cdot[\mathrm{X}^{2-}]}=1.4_2\times10^2$$

$$(K^{\mathrm{X}}_{\mathrm{PbX}})_{\mathrm{IDA}}=\frac{[\mathrm{PbX_2}^{2-}]}{[\mathrm{PbX}^0]\cdot[\mathrm{X}^{2-}]}=6.0_6\times10^3$$

$$(K^{\mathrm{Ac}}_{\mathrm{PbX}})_{\mathrm{Asp}}=\frac{[\mathrm{PbX(Ac)}^-]}{[\mathrm{PbX}^0]\cdot[\mathrm{Ac}^-]}=7.0\times10$$

$$(K^{\mathrm{Ac}}_{\mathrm{PbX}})_{\mathrm{IDA}}=\frac{[\mathrm{PbX(Ac)}^-]}{[\mathrm{PdX}^0]\cdot[\mathrm{Ac}^-]}=3.0_9$$

$$(K^{\mathrm{Ac}}_{\mathrm{PbX(Ac)}})_{\mathrm{Asp}}=\frac{[\mathrm{PbX(Ac)_2}^{2-}]}{[\mathrm{PbX(Ac)}^-]\cdot[\mathrm{Ac}^-]}=1.3_4$$

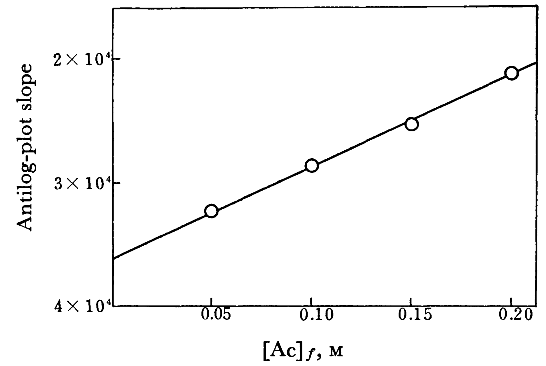

Fig. 4. The plot of antilog-plot slope against the concentration of acetate ion.
IDA system:
Concentration of lead(II) ion=0.50mM, μ=0.30, pH=5.62

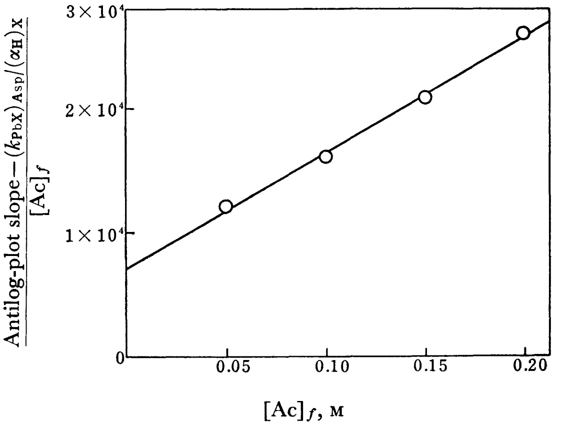

Fig. 5. The plot of (antilog-plot slope $-(k_{\mathrm{PbX}})_{\mathrm{Asp}}/(\alpha_{\mathrm{H}})_{\mathrm{X}})/[\mathrm{Ac}]_f$ against the concentration of acetate ion.
Asp system:
Concentration of lead(II) ion=0.50mM, μ=0.30, pH=5.62

indicates that the concentration of the 1-to-2 complex of Asp or IDA is negligible under the present experimental conditions. In the cases of both Asp and IDA systems, the plot of the antilog-plot −1 divided by $[\mathrm{Ac}]_f$ *versus* $[\mathrm{Ac}]_f$ gives a straight line (Fig. 3). On the basis of Eq. (2), it is very clear that the intercept and the slope of the straight line in Fig. 3 correspond to $K_{\mathrm{PbAc}}/(\alpha_{\mathrm{H}})_{\mathrm{Ac}}$ and $K_{\mathrm{PbAc}}\cdot K^{\mathrm{Ac}}_{\mathrm{PbAc}}/(\alpha_{\mathrm{H}})^2_{\mathrm{Ac}}$ respectively. The K_{PbAc} and $K^{\mathrm{Ac}}_{\mathrm{PbAc}}$ determined from the intercept and the slope of the linear relation in Fig. 3 are given in Table 1. In the case of the IDA system, the plot of the antilog-plot slope *vs.* $[\mathrm{Ac}]_f$ gave a linear relation (Fig. 4). This indicates that, with the IDA anion, the lead(II) ion forms a mixed ligand complex, $\mathrm{PbX(Ac)}^-$, as well as a normal complex, PbX^0. From the slope and intercept of the above linear relation, the $(K_{\mathrm{PbX}})_{\mathrm{IDA}}$ and $(K^{\mathrm{Ac}}_{\mathrm{PbX}})_{\mathrm{IDA}}$ values were determined; they are listed in Table 1. On the other hand, in the case of the Asp system, only the plot of the ratio of antilog-plot minus $(K_{\mathrm{PbX}})_{\mathrm{Asp}}/(\alpha_{\mathrm{H}})_{\mathrm{X}}$ to $[\mathrm{Ac}]_f$ *vs.* $[\mathrm{Ac}]_f$ gave a straight line (Fig. 5). This suggests that, in the case of the Asp system, two mixed ligand complexes, $\mathrm{PbX(Ac)}^-$ and $\mathrm{PbX(Ac)}_2^{2-}$, as well as a normal complex are formed. The $K^{\mathrm{Ac}}_{\mathrm{PbX}}$ and $K^{\mathrm{Ac}}_{\mathrm{PbX(Ac)}}$ values determined from the slope and intercept of the straight line in Fig. 5 are also listed in Table 1. If the above conclusion is correct, the change in the half-wave potential, $\Delta E_{1/2}$, with the change in the hydrogen-ion concentration should be calculable with the aid of Eq. (2). In the case of the IDA system, we used the relation in which the $K_{\mathrm{PbX}}\cdot K^{\mathrm{Ac}}_{\mathrm{PbX}}\cdot K^{\mathrm{Ac}}_{\mathrm{PbX(Ac)}}\cdot[\mathrm{Ac}]^2_f[\mathrm{X}]_f/(\alpha_{\mathrm{H}})^2_{\mathrm{Ac}}\cdot(\alpha_{\mathrm{H}})_{\mathrm{X}}$ in Eq. (2) is not involved. In Table 2, the $\Delta E_{1/2}$ values calculated by using the equilibrium constants determined in this study are given, together with those obtained experimentally. The agreement of the calculated $\Delta E_{1/2}$ values with those determined experimentally can be regarded as satisfactory.

Table 2. The relation between the half-wave potential and the concentration of hydrogen ion

Concentration of lead(II) ion=0.5 mM, μ=0.30, 25°C

(A) Asp system
Concentration of Asp=90.0 mM
Concentration of acetate ion=0.05 M

$E_{1/2}$, V *vs.* SCE	pH	$\Delta E_{1/2}$, mV Calcd	$\Delta E_{1/2}$, mV Obsd
−0.4015	3.71	0	0
−0.4030	4.60	− 1.9	− 1.9
−0.4112	5.50	−13.0	−12.7

(B) IDA system
Concentration of IDA=40.0 mM
Concentration of acetate ion=0.10 M

$E_{1/2}$, V *vs.* SCE	pH	$\Delta E_{1/2}$, mV Calcd	$\Delta E_{1/2}$, mV Obsd
−0.4208	4.50	0	0
−0.4225	4.70	− 4.4	− 4.7
−0.4323	5.01	−11.9	−11.5
−0.4387	5.31	−20.0	−18.0
−0.4443	5.50	−25.2	−23.5

In an alkaline medium, in the cases of both Asp and IDA systems, the plot of the antilog $(\Delta E_{1/2}/0.0296+\log(k_{\mathrm{Pb}^{2+}}/k_{\mathrm{PbX}}))$ value divided by $[\mathrm{X}]_f$ *vs.* $[\mathrm{X}]_f$ gave a straight line with an intercept of a definite value. As was discussed in connection with the polarography of the cadmium(II)-EDTP complex,[4] this fact indicates that the lead(II) ions exist in the forms of PbX^0 and PbX_2^{2-}, and that the electrode reactions can be assumed to be:

$$\begin{array}{l} PbX^0 + 2e^- + nH^+ + Hg \rightleftarrows Pb(Hg) + H_nX^{2-n} \quad (3) \\ \updownarrow \\ PbX_2{}^{2-} \end{array}$$

with the shift of the half-wave potential corresponding to:

$$\Delta E_{1/2} = 0.0296\left[\log\left(\frac{K_{PbX}\cdot[X]_f}{(\alpha_H)_X} + \frac{K_{PbX}\cdot K^X_{PbX}\cdot[X]_f{}^2}{(\alpha_H)_X{}^2}\right) + \log\frac{k_{PbX}}{k_{Pb^{2+}}}\right] \quad (4)$$

where H_nX^{2-n} means incompletely-deprotonated Asp or IDA, where PbX_2^{2-} means a 1 : 2 lead(II)-Asp or -IDA complex, and where K^X_{PbX} is the second successive formation constant of the lead(II)-Asp or -IDA complex. From the slopes and intercepts of the straight lines in Fig. 6, the K_{PbX} and K^X_{PbX} values were determined (Table 1). The K_{PbX} values thus determined agreed well with those estimated in an acid solution. If the electrode reaction in an alkaline medium is given by Eq. (3), the K_{PbX} and K^X_{PbX} thus determined should explain satisfactorily the change in the half-wave potential with the change in the hydrogen-ion concentration. The $\Delta E_{1/2}$ values calculated with the aid of Eq. (4) by using the K values in Table 1 and those determined experimentally are listed in Table 3. A good agreement between them could be observed.

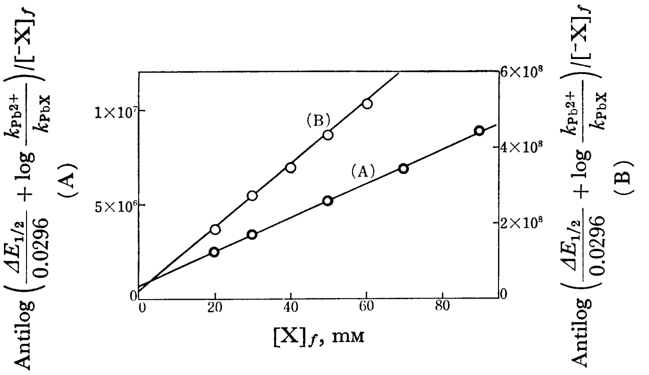

Fig. 6. The plot of antilog $(\Delta E_{1/2}/0.0296 + \log(k_{Pb^{2+}}/k_{PbX}))/[X]_f$ against the concentration of uncomplexed Asp or IDA.
Concentration of lead (II) ion=0.50mM, μ=0.30, 25°C
A : Asp system, pH=9.70
B : IDA system, pH=9.50

The K_{PbAc} and K^{Ac}_{PbAc} values determined in the IDA solution agreed well with those obtained in the Asp solution. They also agree well with those reported by Tanaka and Kato.[5] Here, we can mention that the K^{Ac}_{PbX} and $K^{Ac}_{PbX(Ac)}$ values are all smaller than K_{PbAc} and K^{Ac}_{PbAc}. This is not unreasonable, because the steric and electrostatic effects of coordinated Asp and IDA will reduce the stability of the mixed ligand complexes. The formation constants of the lead(II)-IDA complexes are fairly much larger than those of the Asp complexes. This may be ascribable to the rigid and stable five-membered ring of the IDA complex. It should also be mentioned that, although the Asp anion can from two mixed ligand complexes, the IDA anion can form only one mixed ligand complex, $PbX(Ac)^-$. This fact can be explained well by assuming that the Asp anion acts as a bidentate ligand while the IDA anion acts as a tridentate ligand. As was discussed in the polarographic study of the complex formation reaction of EDTP with the cadmium(II) ion,[4] the assumption that the Asp anion which has a propionate group acts as a bidentate ligand is not unreasonable. Even if the Asp anion acts as a tridentate ligand, from the electronic point of view it can be expected that the lead(II)-Asp complex with a less rigid six-membered ring can be interact with an acetate ion and give a mixed ligand complex more easily than can a rigid IDA complex. In order to describe the properties of the Asp anion as a ligand in detail, further systematic investigations should be conducted.

TABLE 3. THE RELATION BETWEEN THE HALF-WAVE POTENTIAL AND THE CONCENTRATION OF HYDROGEN ION

Concentration of lead(II) ion=0.50 mM, μ=0.30, 25°C

(A) Asp system
Concentration of Asp=70.0 mM

$E_{1/2}$, V *vs.* SCE	pH	$\Delta E_{1/2}$, mV	
		Calcd	Obsd
−0.477	8.35	0	0
−0.494	8.86	−20.3	−17.0
−0.513	8.93	−37.3	−34.0
−0.525	9.70	−47.5	−48.0
−0.537	10.35	−56.4	−60.0

(B) IDA system
Concentration of IDA=50.0 mM

$E_{1/2}$, V *vs.* SCE	pH	$\Delta E_{1/2}$, mV	
		Calcd	Obsd
−0.553	8.76	0	0
−0.562	9.08	− 8.9	− 9.0
−0.577	9.54	−21.9	−24.0
−0.583	9.80	−30.4	−30.0

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[4] M. Kodama and Y. Tominaga, This Bulletin, **42**, 2267 (1969).

[5] N. Tanaka and K. Kato, This Bulletin, **33**, 417 (1960).