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# Metal(II) Complexes of Ethylenediaminemonoacetic Acid (EDMA). Polarographic Studies of Cadmium(II) and Lead(II)-EDMA Complexes

Yuki Fujii, Teiko Ueda and Mutsuo Kodama

*Department of Chemistry, Ibaraki University, Mito, Ibaraki*

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In the present paper, the d.c. polarographic behavior of cadmium(II) and lead(II) ions in ethylenediaminemonoacetate (EDMA) solutions was studied systematically. Since these metal(II) ions in an EDMA solution behave reversibly in a polarographic electrolysis, the compositions and the stability constants of cadmium(II)- and lead(II)-EDMA complexes could be estimated successfully from the shift of the half-wave potential of these metal(II) ions due to the complex formation with EDMA. The cadmium(II) ion was found to form complexes of 1-to-1 and 1-to-2 compositions with EDMA, and the electrode reaction mechanism was established to be:

$$\begin{tikzcd} CdX^+ + 2e^- + nH^+ + Hg = Cd(Hg) + H_nX^{n-1} \arrow[d, shift left] \\ CdX_2 \arrow[u, shift left] \end{tikzcd}$$

The successive formation constants of cadmium(II)-EDMA complexes, $(K_1)_{CdX}$ and $(K_2)_{CdX}$, were determined to be $3.01 \times 10^8$ and $5.65 \times 10^4$ respectively. On the other hand, the lead(II) ion forms only one complex with 1-to-1 composition. In the presence of the chloride ion, the lead(II) ion was found to form a mixed ligand complex involving the chloride ion as well as a normal complex, $PbX^+$, and the electrode reaction could be formulated as:

$$\begin{tikzcd} PbX^+ + 2e^- + nH^+ + Hg = Pb(Hg) + H_nX^{n-1} \arrow[d, shift left] \\ PbXCl^0 \arrow[u, shift left] \end{tikzcd}$$

The equilibrium constants, $(K_1)_{PbX}(=[PbX^+]/([Pb^{2+}]\cdot[[X^-]))$ and $K^{Cl}_{PbX}(=[PbXCl^0]/([PbX^+]\cdot[Cl^-]))$, were determined to be $1.69 \times 10^8$ and $1.01 \times 10$ respectively. The effect of the zinc(II) ion on the half-wave potential of the cadmium(II) ion in an EDMA solution was also studied. From the positive shift of the half-wave potential due to the presence of the zinc(II) ion, the formation constant of the zinc(II)-EDMA complex with a 1-to-1 composition was estimated to be $1.58 \times 10^8$.

Polarographic studies have been made extensively by numerous investigators on the metal complexes of aminopolycarboxylic acids.[1-4] Generally, it has been accepted that cadmium(II) and lead(II) complexes of aminopolycarboxylic acids which have acetic acid groups behave irreversibly in a polarographic electrolysis.[1-3,5] In a previous paper,[6] we ourselves reported that although ethylenediaminetetrapropionic acid (EDTP) has four carboxylate groups and two amino groups, the cadmium(II) ion forms complexes of 1-to-1 and 1-to-2 compositions with EDTP and undergoes a reversible two-electron reduction at the dropping mercury electrode. The formation of the cadmium(II)-EDTP complex with a 1-to-2 composition may indicate that only one propionate group and two amino groups of EDTP anion act as the electron-donating groups in the complex formation reaction with the cadmium(II) ion. Whether or not the reversible nature of the cadmium(II)-EDTP complex can be related to its characteristic structure seems to be very interesting. Therefore, to get much fuller and more accurate information about the above subject, we tried to study the polarographic behavior of the cadmium(II) ion in an ethylenediaminemonoacetic acid (EDMA) which has only one acetate group and compared it with that in the EDTP solution. This attempt was also important in establishing a precise description of the properties of EDMA as a ligand. In this paper, we studied thoroughly the d.c. polarographic

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[3] Y. Koike and H. Hamaguchi, *J. Inorg. Nucl. Chem.*, **29**, 473 (1967).

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behavior of cadmium(II) and lead(II) ions in the EDMA and determined the solution equilibria between EDMA and these ions. The effect of the zinc(II) ion on the polarographic behavior of the cadmium(II) ion in the EDMA solution was also investigated.

## Experimental

**Reagents.** All the chemicals were of an analytical reagent grade and were used without further purification. The standard solution of cadmium(II) perchlorate was prepared by dissolving pure metallic cadmium in perchloric acid (1+2). Its concentration was determined by EDTA titration, using Eriochrom Black T as the indicator.[7] The methods of the preparation and standardization of the zinc(II) perchlorate solution have been given previously.[8] The standard solution of lead(II) nitrate was prepared by dissolving a known amount of lead nitrate in redistilled water. The preparation and purification of EDMA dihydrochloride were also described in a previous paper.[9]

**Apparatus and Experimental Procedures.** All the apparatus (polarographs and a glass electrode pH meter) and the experimental procedures employed have been described previously.[4] The rate of the flow of mercury, $m$, and the drop time, $t_d$, of the dropping mercury electrode used in the present study were 0.839 mg/sec and 3.92 sec respectively at a mercury height of 60 cm in an air-free 0.10 M acetate buffer solution ($\mu$=0.20) of pH 4.80 at 0.0 V *vs.* SCE.

## Results and Discussion

**D. C. Polarographic Behavior of the Cadmium(II) Ion in an Ethylenediaminomonoacetate Solution.** The polarographic behavior of the cadmium(II) ion in an EDMA solution with an ionic strength of 0.20 was studied in the pH range from 6.00 to 7.00. In this study, no buffer reagent was used, because the sample solutions always contained a large excess of uncomplexed EDMA and had enough buffer capacity to maintain the pH value of the solution constant. Under the above pH conditions, the cadmium(II) ion in the EDMA solution invariably gave a single well-difined polarographic wave (Fig. 1). Although the results are not given here, its wave height was exactly proportional to the square-root of the effective mercury pressure on the dropping mercury electrode and to the bulk concentration of the cadmium(II) ion. The log-plot analysis of the polarogram gave linear relations with reciprocal slopes falling into the range from 33 to 37 mV. The results will not be shown here. From the above experimental facts, it can be concluded that the cadmium(II) ion in the EDMA solution undergoes a two-electron reversible reduction at the mercury electrode. Therefore, the solution equilibria between the cadmium(II) ion and EDMA could be determined successfully by the conventional polarographic method employed previously.[6,10-12] As was mentioned in a previous paper,[4] an EDMA anion $X^-$ can be effected to act as a tridentate ligand. Hence, the cadmium(II) ion will also form complexes with 1-to-1 and 1-to-2 compositions, $CdX^+$ and $CdX_2^0$. If both 1-to-1 and 1-to-2 complexes are formed, the electrode reaction of the cadmium(II) ion in the EDMA solution at the DME can be assumed to be:

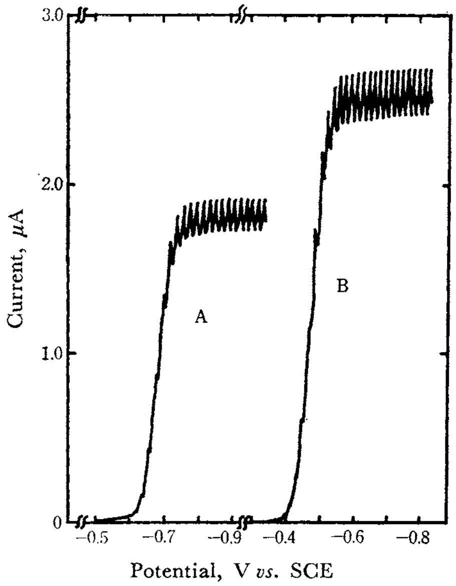

Fig. 1. D.C. polarograms of cadmium(II) and lead(II) ions in the EDMA solution.
A: Concentration of cadmium(II) ion=0.371 mM
Concentration of uncomplexed EDMA=20.0 mM
Concentration of chloride ion=40.0 mM
25°C, $\mu$=0.20, pH=6.95
B: Concentration of lead(II) ion=0.50 mM
Concentration of uncomplexed EDMA =15.0 mM
Concentration of chloride ion=60.0 mM
25°C, $\mu$=0.20, pH=6.45

$$\begin{array}{l} CdX^+ + 2e^- + nH^+ + Hg = Cd(Hg) + H_nX^{n-1} \\ \;\;\rightleftarrows \\ CdX_2^0 \end{array} \qquad (1)$$

where $H_nX^{n-1}$ indicates protonated EDMA species.

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7) W. Biedermann and G. Schwarzenbach, *Chimia*, **2**, 56 (1948).

8) M. Kodama and H. Ebine, This Bulletin, **40**, 1857 (1967).

9) Y. Fujii, E. Kyuno and R. Tsuchiya, *ibid.*, **43**, (1970), in press.

10) M. Kodama, T. Noda and M. Murata, *ibid.*, **41**, 354 (1968).

11) M. Kodama and Y. Tominaga, *ibid.*, **42**, 394 (1969).

12) M. Kodama and Y. Tominaga, *ibid.*, **42**, 724 (1969).

Consequently, as was discussed in connection with the d.c. polarography of the copper(II) ion in an EDMA solution,[4] the shift of the half-wave potential of the cadmium(II) ion due to the complex formation with EDMA can be derived thermodynamically as:

$$\Delta E_{1/2} = (E_{1/2})_{\mathrm{Cd}^{2+}} - (E_{1/2})_{\mathrm{CdX}}$$
$$= 0.0296\left[\log\left(\frac{(K_1)_{\mathrm{CdX}}}{(\alpha_{\mathrm{H}})_{\mathrm{X}}}\cdot[\mathrm{X}]_f + \frac{(K_1)_{\mathrm{CdX}}(K_2)_{\mathrm{CdX}}}{(\alpha_{\mathrm{H}})_{\mathrm{X}}{}^2}\right)\cdot[\mathrm{X}]_f{}^2 + \log\frac{k_{\mathrm{CdX}}}{k_{\mathrm{Cd}^{2+}}}\right] \tag{2}$$

where $(E_{1/2})_{\mathrm{CdX}}$, $(E_{1/2})_{\mathrm{Cd}^{2+}}$, $k_{\mathrm{Cd}^{2+}}$, $k_{\mathrm{CdX}}$ and $(\alpha_{\mathrm{H}})_{\mathrm{X}}$ have their usual meanings.[13] $[\mathrm{X}]_f$ and $(K_i)$ in Eq. (2) denote the concentration of uncomplexed EDMA and the successive formation constants of cadmium(II)-EDMA complexes.

Equation (2) clearly indicates that when solution's pH is kept constant, the plot of antilog $(\Delta E_{1/2}/0.0296+\log(k_{\mathrm{Cd}^{2+}}/k_{\mathrm{CdX}}))/[\mathrm{X}]_f$ against $[\mathrm{X}]_f$ will give a linear relation the slope and the intercept of which will correspond to $(K_1)_{\mathrm{CdX}}(K_2)_{\mathrm{CdX}}/(\alpha_{\mathrm{H}})_{\mathrm{X}}{}^2$ and $(K_1)_{\mathrm{CdX}}/(\alpha_{\mathrm{H}})_{\mathrm{X}}$ respectively. This relation was examined experimentally at pH 6.95. A typical linear relation is shown in Fig. 2. From the intercept and the slope of the linear relation in Fig. 2, the $(K_1)_{\mathrm{CdX}}$ and $(K_2)_{\mathrm{CdX}}$ values were estimated to be $3.01\times10^8$ and $5.65\times10^4$ respectively. The formation of a mixed ligand complex involving the chloride ion could be ruled out, because when the other experimental conditions were kept constant, the half-wave potential was independent of the chloride-ion concentration. If the above conclusion is correct, the dependence of the half-wave potential on the solution pH can be estimated exactly with the aid of Eq. (2) and using the $(K_1)_{\mathrm{CdX}}$ and $(K_2)_{\mathrm{CdX}}$ values determined. The pH dependence of the half-wave potential was calculated and compared with that observed experimentally (Table 1). The agreement of the caluculated values with those determined experimentally can be regarded as satisfactory. This agreement clearly gives strong support to the electrode reaction mechanism proposed by the present authors.

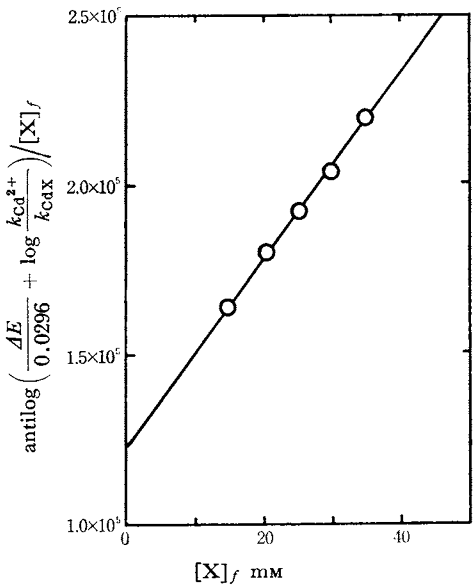

Fig. 2. Determination of successive formation constants of cadium(II)-EDMA complexes.
Concentration of cadmium(II) ion=0.371 mM
25°C, $\mu$=0.20, pH=6.95

Table 1. The effect of pH on the half-wave potential

$\mu$=0.20, 25°C
Concentration of cadmium(II) ion=0.371 mM
Concentration of uncomplexed EDMA=20.0 mM

| pH | Half-wave potential V *vs.* SCE | $\Delta E_{1/2}$, mV Obsd | $\Delta E_{1/2}$, mV Calcd |
|---|---|---|---|
| 6.00 | $-0.603_0$ | 0 | 0 |
| 6.41 | $-0.626_5$ | $23._5$ | 21.8 |
| 6.94 | $-0.665_0$ | $62._0$ | 56.0 |

The effect of the zinc(II) ion on the half-wave potential of the cadmium(II) ion in the EDMA solution was also studied. The cadmium(II) ion in the EDMA solution containing the zinc(II) ion was also found to behave reversibly in a polarographic sense. The log-plot examination at pH's lower than 7.5 gave linear relations with reciprocal solpes falling in the rang from 30 to 33 mV. The results are not shown here. When the total concentration of the zinc(II) ion added, $[\mathrm{Zn(II)}]_t$, is larger than that of EDMA, $[\mathrm{X}]_t$, and when all the EDMA species in the solution exist in the form of $\mathrm{ZnX}^+$, the concentration of the uncomplexed cadmium(II) ion can be given by:

$$[\mathrm{Cd}^{2+}] = \frac{[\mathrm{Cd(II)}]_t}{1+\dfrac{(K_1)_{\mathrm{CdX}}}{(K_1)_{\mathrm{ZnX}}}\dfrac{[\mathrm{ZnX}^+]}{[\mathrm{Zn}^{2+}]}} \tag{3}$$

where $[\mathrm{Cd(II)}]_t$ is the total concentration of the cadmium(II) ion and where $(K_1)_{\mathrm{ZnX}}$ is the formation constant of $\mathrm{ZnX}^+$. Therefore, the half-wave potential of the cadmium(II) ion in the solution containing an excess of the zinc(II) ion over EDMA can be expressed as:

$$E_{1/2} = E_{\mathrm{Cd}}{}^0 + 0.0296\left[\log\frac{k_{\mathrm{Cd(Hg)}}}{k_{\mathrm{Cd}^{2+}}} + \log\left(1+\frac{(K_1)_{\mathrm{CdX}}}{(K_1)_{\mathrm{ZnX}}}\frac{[\mathrm{X}]_t}{[\mathrm{Zn(II)}]_t-[\mathrm{X}]_t}\right) - \log f_{\mathrm{Cd}^{2+}}\right] \tag{4}$$

The symbols used in Eq. (4) have their usual meanings.[6] Hence, the difference in the half-wave potential between the cadmium(II) aquo complex and the cadmium(II) ion in the solution containing EDMA and the zinc(II) ion can be given approximately by:

$$\Delta E_{1/2} = 0.0296\left[\log\left(1+\frac{(K_1)_{\mathrm{CdX}}}{(K_1)_{\mathrm{ZnX}}}\frac{[\mathrm{X}]_t}{[\mathrm{Zn(II)}]_t-[\mathrm{X}]_t}\right)\right] \tag{5}$$

This relation clearly indicates that the plot of anti log ($\Delta E_{1/2}/0.0296$) *vs.* $[\mathrm{X}]_t/([\mathrm{Zn(II)}]_t\text{-}[\mathrm{X}]_t)$ should give the linear relation with an intercept of unity. This relation was examined experimentally on the solution of pH 6.00. A linear relation could be obtained between the antilog ($\Delta E_{1/2}/0.0296$) and $[\mathrm{X}]_t/([\mathrm{Zn(II)}]\text{-}[\mathrm{X}]_t)$. A typical linear relation is shown in Fig. 3. This fact clearly indicates that, in the presence of an excess amount of the zinc(II) ion, the EDMA species exists exclusively in the form of $\mathrm{ZnX^+}$. From the slope of the above linear relation, $(K_1)_{\mathrm{ZnX}}$ was estimated to be $1.58\times10^8$. This value seems reasonable, for the stability constants of zinc(II) complexes of polyamines and aminopolycarboxylic acids have been reported to be nearly identical with those of corresponding cadmium(II) complexes.[13]

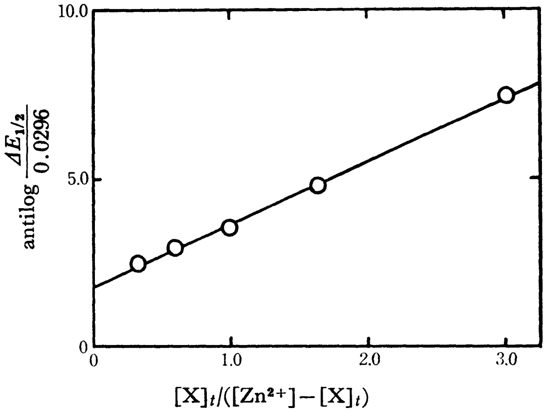

Fig. 3. Determination of formation constant of zinc(II)-EDMA complex.
Concentration of cadmium(II) ion=0.371 mM
Concentration of zinc(II) ion=40.0 mM
Concentration of acetate ion=0.10 M
25°C, $\mu$=20, pH=6.00

**D. C. Polarographic Behavior of the Lead(II) Ion in an EDMA Solution.** The d.c. polarographic behavior of the lead(II) ion in an EDMA solution was also studied in the pH range from 6.50 to 8.50. The lead(II) ions in the EDMA solution also gave a well-defined single wave (Fig. 1), the height of which was exactly proportional to the square-root of the effective pressure on the DME and to the bulk lead(II) ion concentration. Under the present experimental conditions, the log-plot examination invariably gave linear relations with reciprocal slopes falling into the range from 30 to 33 mV. Therefore, the lead(II) ions in the EDMA solution can also be concluded to undergo a two-electron reversible reduction. The lead(II) ion has been reported to form only the complex of a 1-to-1 composition with nitrilotriacetic acid (NTA).[13] This fact clearly indicates that the coordination number of the lead(II) ion is four under the usual experimental conditions. For this reason, in the presence of the chloride ion, the lead(II) ion can be expected to form a normal complex with a 1-to-1 composition, $\mathrm{PbX^+}$, and a mixed ligand complex involving the chloride ion, $\mathrm{PbXCl^0}$, with EDMA. If the lead(II) ion in the EDMA solution containing the chloride ion form a mixed ligand complex as well as a normal complex, the electrode reaction of the lead(II) ion at the mercury electrode can be assumed to be:

$$\begin{array}{l}\mathrm{PbX^+} + 2e^- + n\mathrm{H^+} + \mathrm{Hg} = \mathrm{Pb(Hg)} + \mathrm{H}_n\mathrm{X}^{n-1} \\ \Updownarrow \\ \mathrm{PbXCl^0}\end{array} \tag{6}$$

Consequently, the shift of the half-wave potential of the lead(II) ion due to the complex formation with EDMA can be given by:

$$\Delta E_{1/2} = 0.0296\left[\log\frac{(K_1)_{\mathrm{PdX}}}{(\alpha_{\mathrm{H}})_{\mathrm{X}}}(1+K^{\mathrm{Cl}}_{\mathrm{PbX}}[\mathrm{Cl^-}]) + \log[\mathrm{X}]_f + \log\frac{k_{\mathrm{PbX}}}{k_{\mathrm{Pb^{2+}}}}\right] \tag{7}$$

where $k_{\mathrm{Pb^{2+}}}$ and $k_{\mathrm{PbX}}$ are the diffusion current constants of the lead(II)-aquo and -EDMA complexes respectively, and where $(K_1)_{\mathrm{PbX}}$ and $K^{\mathrm{Cl}}_{\mathrm{PbX}}$ are defined thusly: $(K_1)_{\mathrm{PbX}}=[\mathrm{PbX^+}]/[\mathrm{Pb^{2+}}]\cdot[\mathrm{X^-}]$ and $K^{\mathrm{Cl}}_{\mathrm{PbX}}=[\mathrm{PbXCl^0}]/[\mathrm{PbX^+}]\cdot[\mathrm{Cl^-}]$.

Equation (7) clearly indicates that, if the mixed ligand complex, $\mathrm{PbXCl^0}$, is also formed, the plot of the anitilog($\Delta E_{1/2}/0.0296+\log k_{\mathrm{Pb^{2+}}}/k_{\mathrm{PbX}}-\log[\mathrm{X}]_f$) against the concentration of the uncomplexed chloride ion, $[\mathrm{Cl^-}]$, should give a linear relation when the other experimental conditions are kept constant. This relation was examined experimentally on the solution of pH 6.45. A linear relation was found between the antilog$[\Delta E_{1/2}/0.0296+\log k_{\mathrm{Pb^{2+}}}/k_{\mathrm{PbX}}-\log[\mathrm{X}]_f]$ and $[\mathrm{Cl^-}]$ (Fig. 4). From the slope and the intercept of the above linear relation, the $K^{\mathrm{Cl}}_{\mathrm{PbX}}$ and $(K_1)_{\mathrm{PbX}}$ values were estimated to be $1.08\times10$ and $1.69\times10^8$ respectively.

Equation (7) also shows that when the other experimental conditions are kept constant, the following relation should hold between the shift of the half-wave potential and $\log(\alpha_{\mathrm{H}})_{\mathrm{X}}$:

$$\frac{\Delta E_{1/2}}{\Delta\log(\alpha_{\mathrm{H}})_{\mathrm{X}}} = 29.6\ \mathrm{mV} \tag{8}$$

This relation was also examined experimentally. The results are given in Table 2. The shift of the half-wave potential calculated with the aid of Eq. (8) agreed well with that observed. Using the

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[13] L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London (1964).

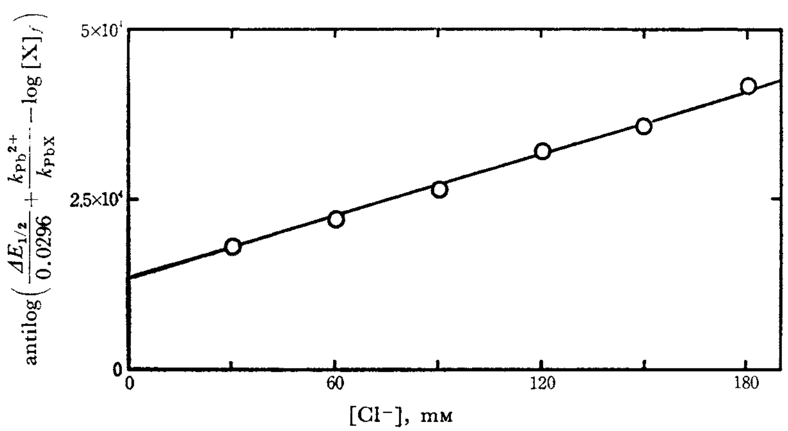

Fig. 4. Determination of formation constants of lead(II)-EDMA complexes.
Concentration of lead(II) ion=0.50 mM
Concentration of uncomplexed EDMA=15.0 mM
25°C, $\mu$=0.20, pH=6.45

TABLE 2. THE EFFECT OF pH ON THE HALF-WAVE POTENTIAL

$\mu$=0.20, 25°C
Concentration of lead(II) ion=0.50 mM
Concentration of uncomplexed EDMA=20.0 mM

| pH | Half-wave potential V *vs.* SCE | $\Delta E_{1/2}$, mV | |
|---|---|---|---|
| | | Obsd | Calcd |
| 6.75 | $-0.456_7$ | 0 | 0 |
| 7.29 | $-0.476_2$ | $19._5$ | 19.6 |
| 7.85 | $-0.493_3$ | $36._6$ | 39.4 |
| 8.36 | $-0.509_0$ | $52._3$ | 55.1 |

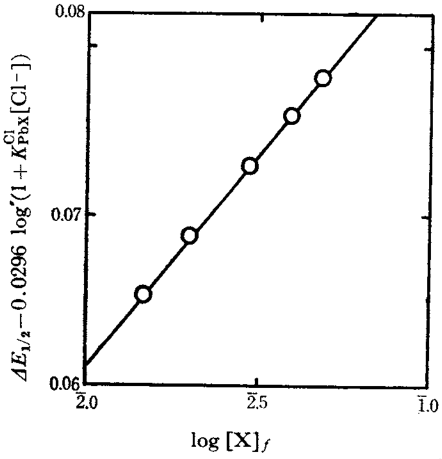

Fig. 5. The plot of $\Delta E_{1/2}-0.0296(1+K^{Cl}_{PbX}\cdot[Cl^-])$ against log $[X]_f$.
Concentration of lead(II) ion=0.50 mM
25°C, $\mu$=0.20, pH=6.45

$K^{Cl}_{PbX}$ value determined, the effect of the concentration of the uncomplexed EDMA on the half-wave potential of the lead(II) ion was also studied. Equation (7) shows that when the solution pH is kept constant, the plot of $\Delta E_{1/2}-0.0296\log(1+K^{Cl}_{PbX}\times[Cl^-])$ against log $[X]_f$ should give a linear relation. This was also examined satisfactorily. The results obtained are shown in Fig. 5. From the above results and discussion, it can safely be concluded that, under the present experimental conditions, the lead(II) ion forms $PbX^+$ and $PbXCl^0$ and the electrode reaction mechanism of the lead(II) ion in an EDMA solution can be given by Eq. (6).

As has been stated above, both cadmium(II) complexes of EDTP and EDMA undergo a reversible two-electron reduction at the dropping mercury electrode. The former complex may contain two six-membered rings involving a metal-oxygen bond, while the latter may contain two five-membered rings involving a metal-oxygen bond. Therefore, the reversible behavior of the cadmium(II)-EDTP complex can hardly be ascribed to the structure of EDTP, in which all acetate groups of ethylenediaminetetraacetate are replaced by propionate groups to give terminal rings of six rather than five members. It should also be mentioned here that cadmium(II)-aminopolycarboxylate complexes which have larger stability constants behave irreversibly, whereas those which have smaller stability constants behave reversibly. Generally, the larger stability constant is considered to correspond to the greater affinity of the ligand for the metal ion. The greater affinity for the metal ion will, then, produce the more pronounced change in the electronic structure of the metal ion. On the basis of the above discussion, the cadmium(II) ion in the EDTP and EDMA complexes may be said to have an electronic structure not significantly different from that of the cadmium(II) aquo complex, which undergoes a typical reversible reduction. This may also account for the reversible behavior of the cadmium(II)-EDTP and -EDMA complexes.

Since the cadmium(II) ion can form complexes of a 1-to-2 composition with EDTP and EDMA, in both cadmium(II) complexes two ligands are considered to be attached to each cadmium(II) ion with four nitrogens and two oxygens. Considering the well-known fact that the cadmium(II)-amine complex behaves reversibly in a polarographic electrolysis,[14] this may mean that the nature and the number of donor atoms also play an important role in the determination of the polarographic behavior of cadmium(II)-aminopolycarboxylate complexes. In order to describe the precise relation between the polarographic behavior of the cadmium(II)-aminopolycarboxylate complex and its structure, however, further systematic investigations should be conducted.

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14) L. Meites, *J. Amer. Chem. Soc.*, **72**, 2293 (1950).