Polarographic and emf Studies of the Reaction between Ethyl Xanthate and Cadmium(II) ion

Polarographic and emf Studies of the Reaction between Ethyl Xanthate and Cadmium (II) ion*

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Synopsis

The reduction of cadmium (II) ion in the presence of excess of potassium ethyl xanthate was studied on the dropping mercury electrode, and emf measurements were carried out by using cadmium amalgam electrode.

The d. c. polarogram gave a well-defined wave which corresponded to the one of reduction of cadmium (II) ion to cadmium amalgam. By employing polarographic method, the composition of a complex between ethyl xanthate and cadmium(II) ions was found to be $Cd(EX)_4^{2-}$ $(\beta_4 = 4 \times 10^{11})$.

From emf measurements, nearly the same results were obtained without any assumption, and the absence of $Cd(EX)_3^-$ was suggested.

I. Introduction

Reports have been made by several authors on the polarographic behaviors of alkali ethyl xanthate (MEX)[1~8] but these reports dealt only with the oxidation wave of the xanthate ions (EX^-) which might be produced as the result of the anodic dissolution of mercury, and the studies of the reduction wave of metal complexes of the xanthate have been left untouched because of the formation of the insoluble metallic salts in aqueous solutions. Owing to these properties, xanthates have been used as mineral flotation reagents and as analytical ones and many investigators who have been concerned with studies of mineral flotation have tried to determine the solubilities of heavy metal xanthates.

Recent progress in coordination chemistry has shown that soluble metallic complexes are found in aqueous solutions besides insoluble ones when the reactions are caused by changing the molar ratios of the reactors. For instance, $Pb(OH)_2$ is an insoluble salt with $K_{sp} = 10^{-16.1}$, but a soluble complex, $Pb(OH)_3^-$ is formed

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* The **169th** report of the Research Institute of Mineral Dressing and Metallurgy.

(1) U. Fujii, J. Mining Metal. Inst. Japan, **70** (1954), 99.

(2) S. Sun and R.T. Holymann, Anal. Chem., **29** (1957), 1298.

(3) S.G. Salamy and J.C. Nixon, Australian J. Chem., **7** (1954), 146.

(4) I.M. Paulova, Khim i Khim Tekhnol., Alma-ata, *Sb.* 2 (1964), 127: C.A., **64** (1966), 4256th.

(5) A.J. Lyfield, C.A., **62** (1965), 15809f.

(6) P. Winfried, Freiferger Forshungsh, A302 (1963), 53: C.A., **61** (1964), 4940f.

(7) W. Poetsch and K. Schwave, J. prakt, Chem., **18** (1962), 1: C.A., **57** (1962), 16322f.

(8) M. Cap, A. Drork, and V. Hencil, C.A., **50** (1956), 3160b.

in accordance with the following equation:[9]

$$Pb(OH)_2 + OH^- \rightleftharpoons Pb(OH)_3^- .$$
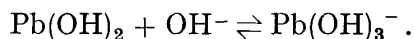
The authors started the investigations with a hope to find the soluble heavy metallic complexes of ethyl xanthate in aqueous solutions hitherto undescribed in literature, to study their properties by concentrating on the nature of sulfur bond with metal ions and to offer some fundamental data to explain the mechnism of mineral flotation.

Majima[10] reported the formation of some soluble metallic complexes of the ethyl xanthate but his findings were limited only to the fact in aceton-water (1:1) solutions. By means of a polarographic and of an emf method we proved the formation of a soluble complex with a formula $Cd(EX)_4^{2-}$ in a reaction between Cd^{2+} and an excess of EX^- in aqueous solution and the results were briefly reported previously.[11] This paper describes the results in detail.

The solubility product constant of bis (ethylxanthogenato) cadmium (II), $Cd(EX)_2$, has been reported to be 5.6×10^{-15} or 2.6×10^{-14}[12,13]. However, this almost insoluble $Cd(EX)_2$ was found to be dissolved in the solution of excess of EX^- to form a tetracoordinate complex, $Cd(EX)_4^{2-}$ and the over-all stability constant of this complex, β_4 was determined to be 4×10^{11} by the polarographic measurements. Also, from the emf measurements, the formation of $Cd(EX)_4^{2-}$ and the absence of a 1:3 complex, $Cd(EX)_3^-$ were suggested, and β_4 was obtained to be 2×10^{11} which was in good agreement with that obtained from the polarographic method.

II. Experimental

KEX was prepared by mixing a solution of potassium hydroxide in an ethyl alcohol with carbon disulfide. The salt was washed in ethyl ether and recrystallized three times from ethyl alcohol by adding ethyl ether. Its purity was confirmed to be $100.0 \pm 0.2\%$ by titrating weighed samples with a standard iodine solution. The cadmium amalgam electrode for the emf measurements containing 15 wt% of cadmium was prepared by mixing mercury (99.999% pure) and cadmium sheet (99.99% pure) in the nitrogen atmospher on a hot plate. All other chemicals used were of a guaranteed reagent grade and were used without further purification. The concentration of cadmium nitrate solution was determined by the volumetric titration with the standardized EDTA solution.

Apparatus: A direct current (d.c.) polarograms were recorded on a Shimazu
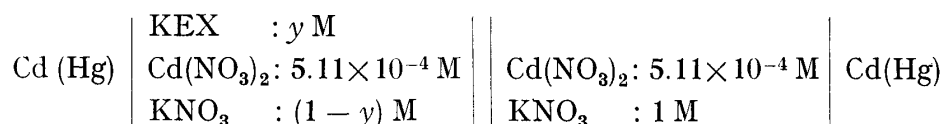
(9)   J.J. Lingane, Chem. Rev., **29** (1941), 1.

(10) H. Majima, Sci. Rep. RITU., A13 (1961), 434.

(11) T. Yamasaki and M. Nanjo, Chem. & Ind., (1966), 1530.

(12) I.A. Kakousky, *Second International Congress of Surface Activity*, Vol. *IV*, edited by J.H. Schulman (1957), 225, Butterworth Scientific Publications.

(13) A.T. Pilipenko, T.P. Vorohenko, E.S. Kudelya and A.P. Kostysina, *Soviet Research on Complex and Coordination Compounds*, Part *II*, p. 1325.

RP-2 Polaro-recorder equipped with an automatic potential scanner and iR compensator with a second reference electrode (Fig. 1–a). The dropping mercury electrode (d.m.e.) employed had an m value of 2.3 mg/sec and a drop time, t_d, of 3.75 sec/drop at –0.50 V vs. SCE in 1 M of deaerated potassium nitrate solution. Gelatin was added as a maximum suppressor by 0.015 wt% in concentration. The emf measured by means of a Shimazu Type K-Potentiometer. The concentration cell employed is shown below:

$$Cd\,(Hg)\ \left|\begin{array}{l} KEX\quad :y\,M \\ Cd(NO_3)_2: 5.11\times10^{-4}\,M \\ KNO_3\quad :(1-y)\,M \end{array}\right|\left|\ \left|\begin{array}{l} Cd(NO_3)_2: 5.11\times10^{-4}\,M \\ KNO_3\quad :1\,M \end{array}\right|\ Cd(Hg)\right.$$

The half-cells were connected simply with an H type salt-bridge as shown in Fig. 1–b. While conducting measurements, a slow stream of nitrogen was passed through the cells. All the measurements were made at an ionic strength, μ, 1.0 and at 25°C. The ionic strength was adjusted with potassium nitrate in the case of aqueous solutions and with sodium perchlorate for 50 vol % of ethyl alcohol aqueous solutions. The measuring solutions were not buffered.
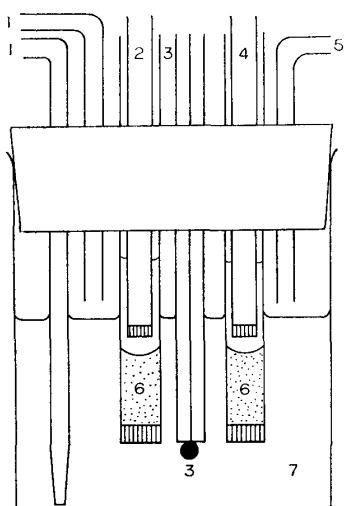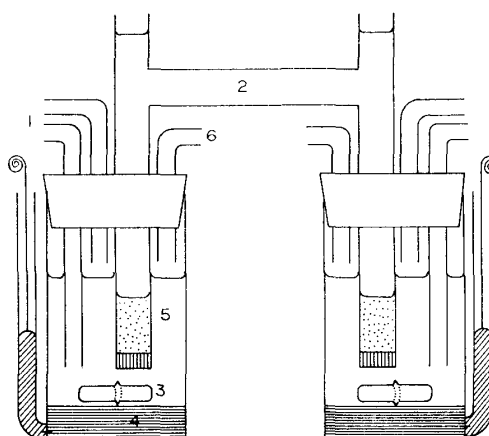

Fig. 1-a.   Fig. 1-b.

Fig. 1–a. Polarographic cell
    1 N_2 gas inlet tube   2 Reference electrode   3 d.m.e.
    4 Electrode for iR drop compensator   5 N_2 gas outlet tube
    6 Agar plug   7 Sample solution
1-b. emf cell
    1 N_2 gas inlet tube   2 H type salt bridge   3 Stirrer
    4 Cadmium amalgam electrode   5 Sample solution   6 N_2 gas outlet tube

III. Results and discussion

1. Polarographic study in aqueous solution. The titration curves of cadmium nitrate with low (1.0×10^{-2} M) and high (5.0×10^{-1} M) concentration of the KEX solutions are presented in Figs. 2 and 3, respectively. As can be seen from Fig.

2, the limiting current i_l, decreased with the formation of the precipitate, and at the equivalent point, the mole ratio $[EX^-]_{add}/[Cd^{2+}]_{add}$. was found to be 2.2, where $[EX^-]_{add}$ and $[Cd^{2+}]_{add}$ mean the concentration of ethyl xanthate and cadmium ion added, respectively. The precipitate obtained was $Cd(EX)_2$.

Analysis obtained Cd: 31.2%, C: 20.5%, H: 3.0%

Calculated for $C_6H_{10}O_2S_4Cd$

Cd: 31.69%, C: 20.3%, H: 2.84%

In the case of the titration with the concentrated KEX solution, the primary-formed precipitate dissolved and gave the constant limiting current at the concentration of EX^- more than 50 times higher than that of cadmium (II) ion, $(6.25 \times 10^{-4}$ M). From Figs. 2 and 3, the formation of $Cd(EX)_2$ and the existence of the soluble species were proved.
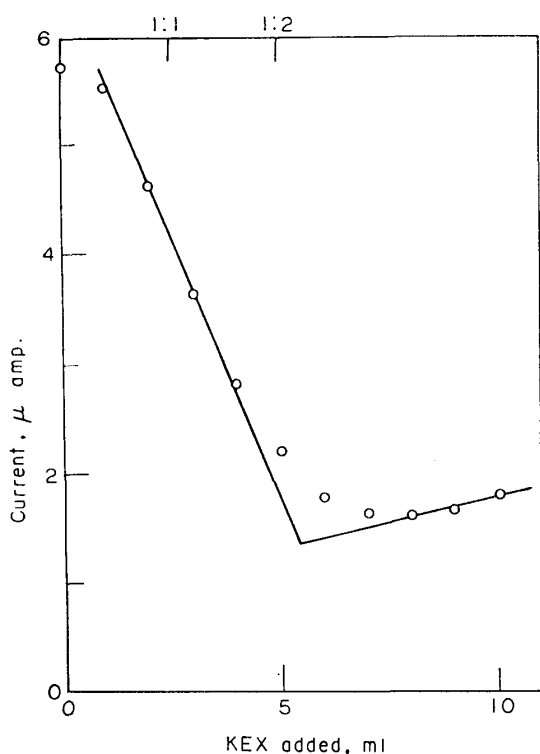

Fig. 2.   Fig. 3.

Fig. 2. Amperometry of $Cd(NO_3)_2$ with dilute KEX solution $(5.0 \times 10^{-1}$ M) at -1.00 V vs. SCE.
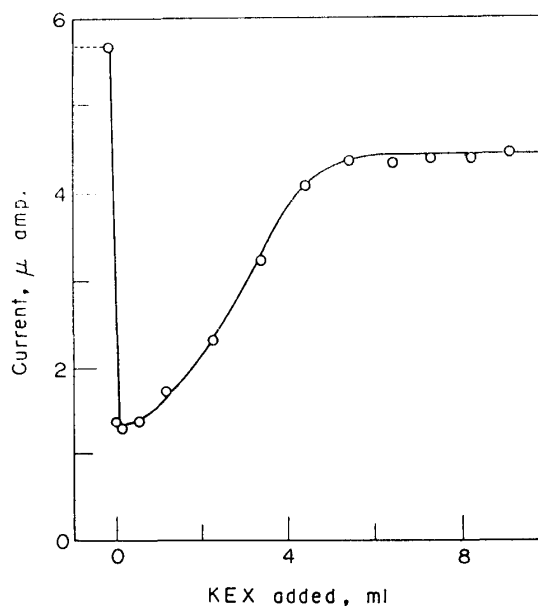
Fig. 3. Amperometry of $Cd(NO_3)_2$ with concentrate KEX solution $(5.0 \times 10^{-1}$ M) at -1.00 V vs. SCE

The current-potential curves of cadmium (II) $(8.33 \times 10^{-4}$ M) obtained in the presence and in the absence of an excess of EX^- are shown in Fig. 4. The well-defined polarograms in the unbuffered solution (pH $9 \sim 10$) were obtained, but in the absence of gelatin a maximum wave was obtained. Fig. 5 presents the limiting current measured at the different height of the mercury reservoir at
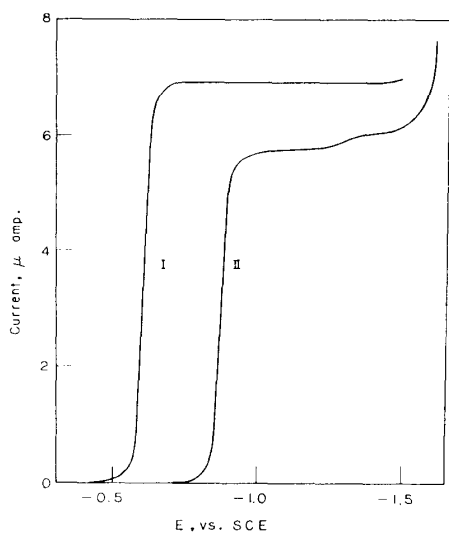
Fig. 4.   Fig. 5.

Fig. 4. Polarograms of $Cd(NO_3)_2$ (8.33×10^{-4}M)
I. KEX: 0,   II. KEX: 2.82×10^{-1} M
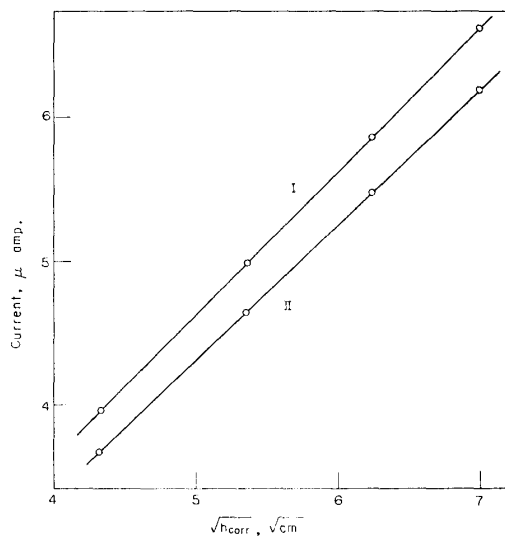
Fig. 5. Effect of pressure of mercury at -1.10 V vs. SCE.
I. KEX: 1.70×10^{-1} M, $Cd(NO_3)_2$: 8.33×10^{-4} M
II. KEX: 8.07×10^{-1} M, $Cd(NO_3)_2$: 8.33×10^{-4} M

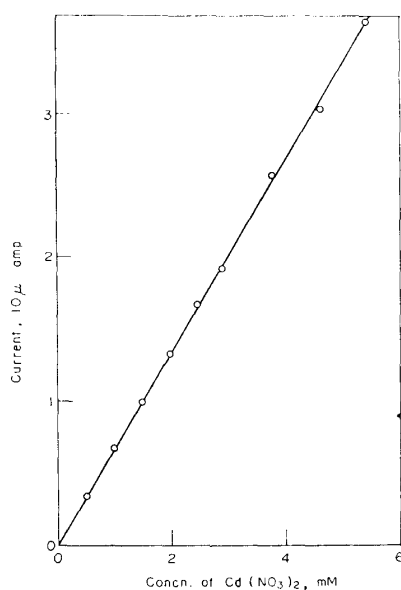Fig. 6.   Fig. 7.

Fig. 6. Calibration curve of $Cd(NO_3)_2$ solution in the presence of KEX (6.75×10^{-1}M) at -1.10V vs. SCE.
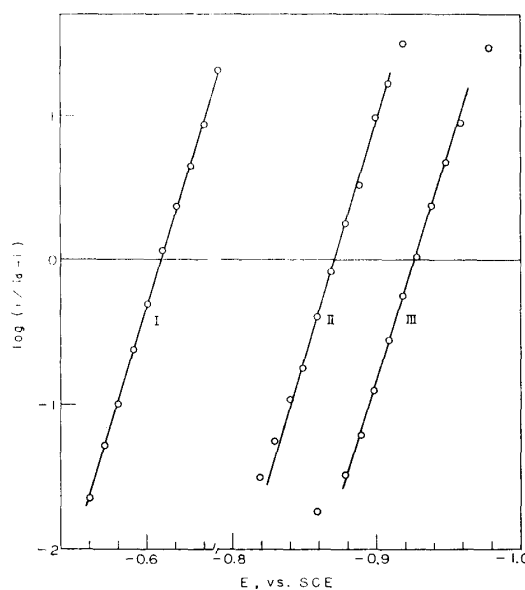
Fig. 7. Relation of log (i/i_d-i) with E

-1.10 V vs. SCE.   From Fig. 6, it was found that the limiting current was propor-
tional to the concentration of the complex ion formed.

The half-wave potential $E_{1/2}$ was found to be independent of the concentration
of the complex.   These results indicate the limiting current is diffusion-controlled.

By plotting $\log i/(i_d-i)$ against the potential, E in Fig. 7, it was suggested that the reaction on d.m.e. was of the two-electron reduction and that $E_{1/2}$ was found to shift to more negative side with increasing concentration of KEX. An average of the slopes of the log plots was found to be 33 mV, which indicates the reduction on d.m.e. was of a reversible two-electron reduction. Under these conditions, the application of the polarographic determination of the stability constants by using the shift of $E_{1/2}$ produced by complex formation is possible.[14]   Equations for the half-wave potentials of the waves obtained when simple ion is reversibly reduced to metal amalgams are shown as follow:
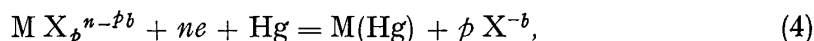
$$M^{n+} + ne + Hg = M(Hg) , \qquad (1)$$
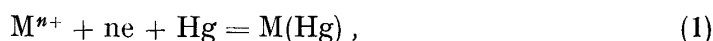
and the half-wave potential, $E_{1/2}$ is given as follow:

$$(E_{1/2})_s = E_s{}^0 - \frac{RT}{nF} \ln\left(- \frac{f_a k_s}{f_s k_a} \right), \qquad (2)$$

where $E_s{}^0$ is the standard potential of the metal ion-metal amalgam couple, f_a and f_s are the activity coefficients of the metal atoms in the amalgam and the metal ions in the solution, k_a is the ratio of the anodic diffusion current to the concentration of metal in the amalgam, and k_s is the ratio of the cathodic diffusion current to the concentration of metal ion in the solution. According to the Ilkovič equation,[14] we have

$$- k_s/k_a = D_s{}^{1/2}/D_a{}^{1/2} , \qquad (3)$$

For the reversible reduction of a complex ion, we have

$$M X_p{}^{n-pb} + ne + Hg = M(Hg) + p X^{-b}, \qquad (4)$$

and the half-wave potential $(E_{1/2})_c$ is given as follow:

$$(E_{1/2})_c = E_s{}^0 - \frac{RT}{nF} \ln \left(- \frac{f_a k_c}{f_c k_a} \right) + \frac{RT}{nF} \ln K_c - \frac{RT}{nF} p \ln C_x f_x \qquad (5)$$

where the subscript c denotes the complex ion, K_c is the overall dissociation constant of the predominating complex $MX_p{}^{n-pb}$, and C_x is the concentration of the ligand X, which is assumed to be so large that it does not vary at the drop surface as the current changes.

Subtracting eq. (2) from (5) yield a description of the difference between the half-wave potentials of the complex and simple metal ions at 25°C;

$$(E_{1/2})_c - (E_{1/2})_s = \frac{0.0591}{n} \left(\log K_c - \log \frac{f_s k_c}{f_c k_s} - p \log C_x f_x \right) \qquad (6)$$

It is tacitly assumed that K_c is much smaller than $C_x{}^p$, so that the concentration of the simple ion and any possible lower complex can be neglected in the presence of the excess of ligand.

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(14)   L. Meites, *Polarographic Techniques* p. 268, second edition, Interscience Pub. New York (1965).

From the eq. (6), it can be used to find a formula of the complex (that is, the value of p) from data on the variation of half-wave potential with ligand concentration, and it is also of service in evaluating the dissociation constant K_c. Differentiation of eq. (6) gives

$$d\,(E_{1/2})_c/d\,(\log C_x) = -\,0.0591\,p/n \qquad (7)$$

provided that the activity coefficients f_s, f_c, and f_x and the liquid-junction potential all remain constant as C_x is varied, and that the ratio k_c/k_s also remains constant.

As long as C_x does not exceed 1M, neither k_c nor k_s is likely to vary greatly. Usually k_c/k_s is constant over a wide range of experimental conditions. The activity coefficients will not almost surely remain constant as an inert electrolyte is replaced by an electrolyte containing X^- even though the ionic strength does not change. Moreover, there will be a variation of the liquid-junction potential. Subject to these assumptions and uncertainties, the value of p can be obtained directly from the slope of a plot in Fig. 8 with ethyl xanthate concentration between 0.2 and 1.0 M.
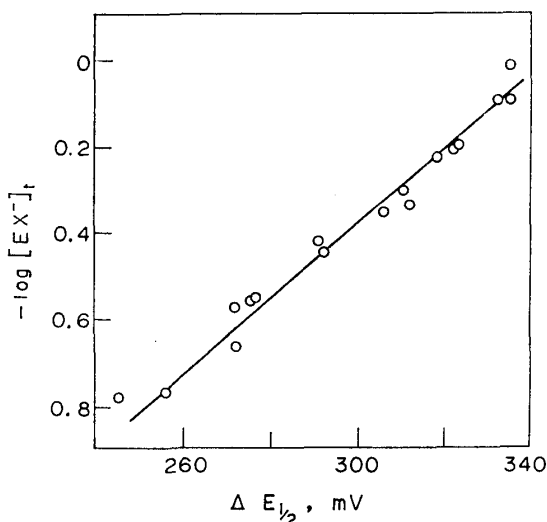

Fig. 8. Relation of $\Delta E_{1/2}$ with log $[EX^-]_t$ 25°C, $\mu=1(KNO_3)$

As can be seen from Fig. 8, a straight line was obtained by the least square method as follows in V:

$$\Delta\,(E_{1/2}) = -\,0.345 - 0.118\log[EX^-]_t \qquad (8)$$

The experimental value of $d\,(E_{1/2})/d\,(\log[EX^-]_t)$ is -0.118 V. Since $n=2$ for the reduction of the cadmium (II) complex to cadmium amalgam, as can be seen from Fig. 7, eq. (7) became

$$-\,0.118 = -\,0.0591\,p/2 \qquad (9)$$

hence $p =4.0$. Consequently, the predominating complex under these conditions

must be $Cd(EX)_4^{2-}$. From the equation for the straight line through the experimental point in Fig. 8, it is found that $(E_{1/2})_c$ is -0.930 V. vs. SCE when the ethyl xanthate concentration is 1.00 M. The half-wave potential of the simple cadmium ion in 1.0 M potassium nitrate free from added ehtyl xanthate is -0.595 V. vs. SCE. It is not reasonable to suppose that the liquid-junction potential between the saturated potassium chloride in the SCE and 1.0 M potassium nitrate will be essentially identical with that between saturated potassium chloride and 1 M potassium ehtyl xanthate. However, on assuming they are identical with each other, eq. (6) may now be written for $[EX^-]_t = 1$ M as follow:

$$(E_{1/2})\,_{c,c_x=1} - (E_{1/2})_s = \frac{0.0591}{n}\left(\log K_c - \log\frac{f_s}{f_c} - \log\frac{k_c}{k_s} - p\log f_x\right) \quad (10)$$

To obtain K_c, it is necessary to evaluate or make some assumption on each of the last three terms on the right hand side of this equation. The ratio k_c/k_s is given according to the Ilkovič equation,[15] by

$$k_c/k_s = D_c^{1/2}/D_s^{1/2} = I_c/I_s\,, \quad (11)$$

so that it was calculated from the corresponding diffusion current constants to be 0.82.

The activity coefficients are more difficult to deal with. About the best approximation that can be made is to describe each of them by the extended Debye-Hückel equation as follow:

$$\log f_i = \frac{0.51\,z_i^2\,\mu^{1/2}}{1 + 0.33\,a_i\,\mu^{1/2}} + B_i\mu \quad (12)$$

Assuming that the distance of the closest approach a_i is equal to the typical value 4.5 Å for each of the ionic species and that the salting-out coefficients B_i are also equal, we have

$$\log\,(f_s/f_c) = (z_c^2 - z_s^2)\,L\,, \quad (13)$$

where

$$L = 0.51\,\mu^{1/2}/(1 + 1.5\,\mu^{1/2})\,. \quad (14)$$

In the case in which z_c^2 and z_s^2 are equal, f_s and f_c will be equal. The activity coefficient of f_x remians not evaluated and f_x has not been obtained.

Assuming it to be a unit, we obtained K_c to be $1/4 \times 10^{11}$ simply by the following equation:

$$\mathit{\Delta}\,(E_{1/2})_{c_x-1} = \frac{0.0591}{n}\,(\log K_c - \log k_c/k_s) \quad (15)$$

From these calculations the species dissolved in the solution is $Cd(EX)_4^{2-}$ in a concentration region of $0.2 \sim 1$M of KEX solutions.

2- Polarographic study in a 50 vol% of ethyl alcohol. $Cd(EX)_2$ is hardly a soluble complex in water but it dissolves easily in organic solvents, e.g. ethyl

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(15) D. Ilkovič, Collection, 6 (1934), 498.
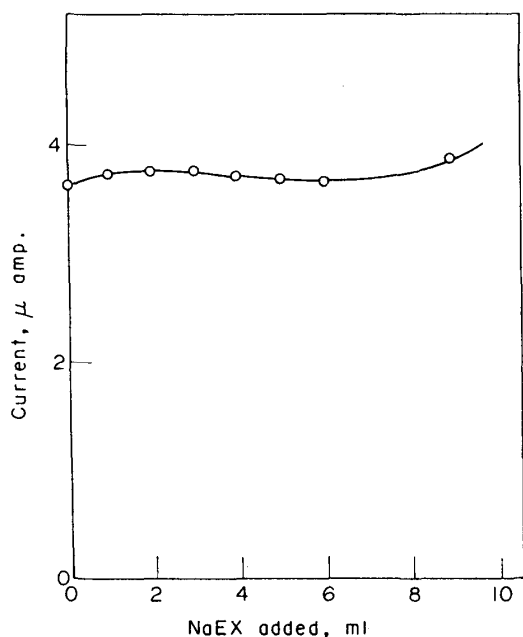
Fig. 9.   Fig. 10.

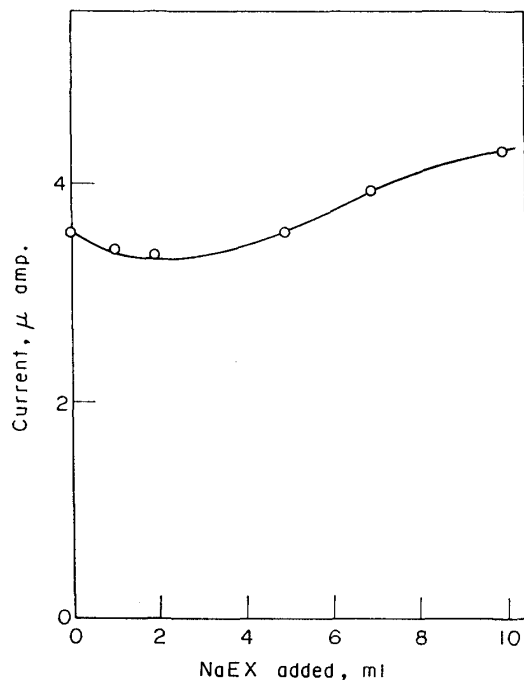Fig. 9. Amperometry of $Cd(NO_3)_2$ with dilute NaEX $(1.0 \times 10^{-2} M)$ 50% EtOH solution at -1.00 V vs. SCE

Fig. 10. Amperometry of $Cd(NO_3)_2$ with concentrate NaEX $(5.0 \times 10^{-1} M)$ 50% EtOH solution at $-1.00V$ vs. SCE

alcohol. This leads us to an assumption that ionic and molecular species formed in organic solvent may be different from those formed in water. $Cd(EX)_2$ dissolved in a 50 vol% ethyl alcohol aqueous solution reached several mMs. The results of amperometric titrations are shown in Figs. 9 and 10. A remarkable decrease in current by the precipitate formation could not be observed and little change in current by the transition from simple ion to complex ion was detected. Thus, the condition required for employing the poralographic method was fully satisfied. As shown in Fig. 11, a straight line obtained can be expressed as follows in V:

$$\varDelta(E_{1/2}) = -0.432 - 0.093 \log [E\ X^-]_t . \qquad (16)$$

This indicates that the coordination number p was 3.3 and the β_3 was 5×10^{14} by employing the value of $(E_{1/2})_s = -0.563$ V. vs. SCE which had been determined experimentally.

The reasons of the formation of $Cd(EX)_3^-$ in a 50 vol % of ethyl alcohol solution and $Cd(EX)_4{}^{2-}$ in aqueous solution at the same concentration of the ligand could not be explained satisfactorily, but it may be one of the reasons why the insoluble $Cd(EX)_2$ in aqueous solution is easily dissolved in a 50 vol% of ethyl alcohol aqueous solution.
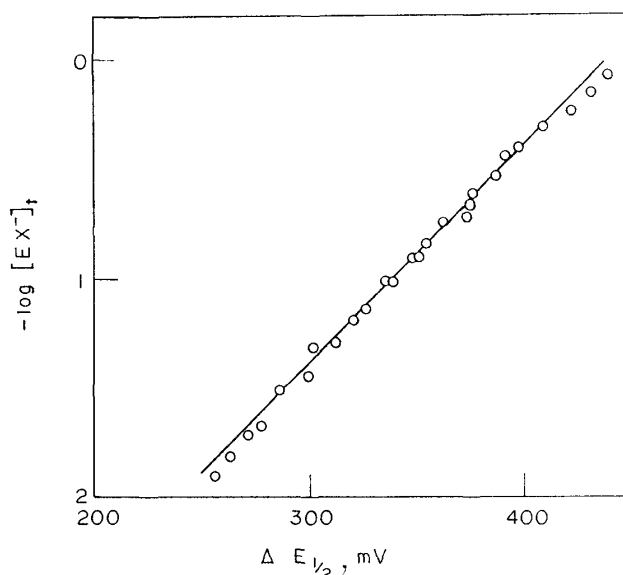
Fig. 11.   Relation of $\Delta E_{1/2}$ with log $[EX^-]_t$ in 50% EtOH solution, 25°C, $\mu = 1$ (NaClO$_4$)

3.   emf study in aqueous solution.   The decrease in activity of Cd(II) ion by the complex formation could be explained by the shift of $E_{1/2}$, but the determinable region of the $E_{1/2}$, was limited to some extent.   The formation of the precipitate resulted in the decrease in the concentration of cadmium (II) ion and in the attachment of the precipitate on the mercury electrode.   Accordingly, measurements of $E_{1/2}$ became impossible.   In these cases, emf method is a useful method and all of the complexes formed under the conditions are expected to be detected. The authors employed cadmium amalgam electrode with an intention to find out complexes other than Cd(EX)$_4^{2-}$ and emf measured was plotted against the time after mixing the cadmium (II) ion and EX$^-$ are shown in Fig. 12.   The constancy of emf within 0.5 mV was attained within two hrs.   In Fig. 13, emf plotted against log $[EX^-]_t$ is shown and the $[EX^-]_t$ was calculated by the following equation:

$$[EX^-]_t = [EX^-]_{add} - [Cd^{2+}]_{ppt}/2 = [EX^-]_{add} - [Cd^{2+}]_{add}/2 \qquad (17)$$

In the case when the precipitate formation is the main reaction, all of the Cd(II) ion added was assumed to be removed as precipitate, and in the concentration region of $[EX^-]_t > 0.4$ M, emf was determined by the following equation that was obtained from the slope shown in Fig. 13 in V;

$$\text{emf} = -0.331 - 0.122 \log [EX^-]_t . \qquad (18)$$

From the slope of the straight line, p and β_4 were determined to be 4.1 and 2×10^{11}, respectively.   These showed good agreement with the data given by the polarographic method.   In the concentration region $[EX^-]_t > 0.4$ M, a straight line with the slope 2.2 was obtained, whose empirical formula was in V;

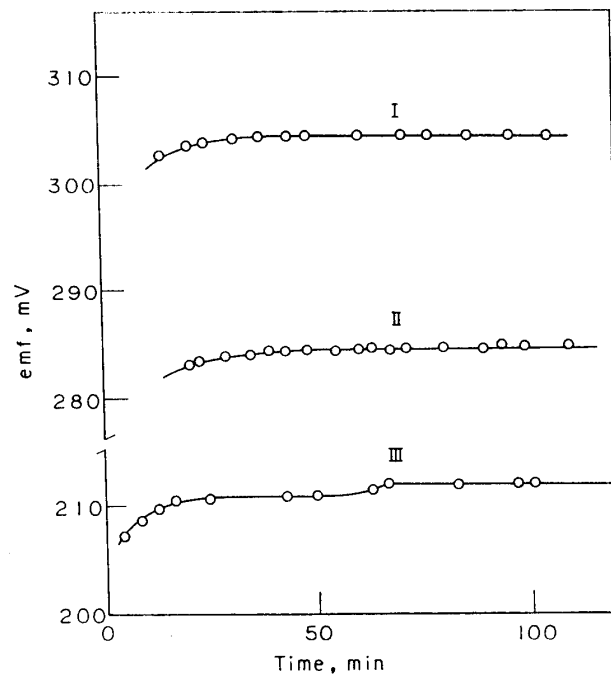$$\text{emf} = -0.303 - 0.066 \log [EX^-]_t . \qquad (19)$$

Fig. 12. Constancy of emf

    I. KEX: 6.20×10^{-1}M   II. KEX: 4.03×10^{-1}M   III. KEX: 4.08×10^{-2}M
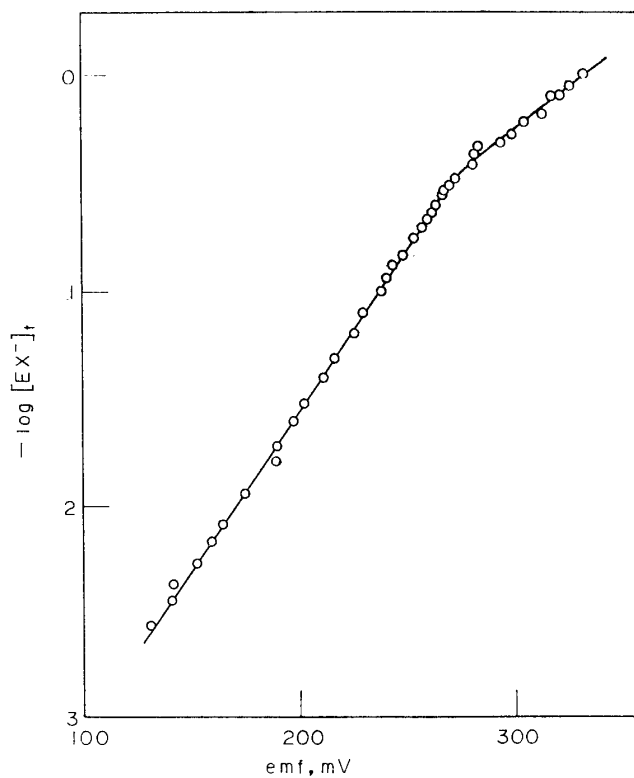
    $Cd(NO_3)_2$: 5.11×10^{-4}M

Fig. 13. Relation of emf with log $[EX^-]_t$, 25°C, $\mu = 1(KNO_3)$

In the region the main product was the precipitate $(Cd(EX)_2)$ and the concentrations of the dissolved species obeyed the law of solubility products.   We failed to find out the region where 1:3 complex, $Cd(EX)_3^-$, was formed predominantly.

Kodama and Hayashi[16] obtained nearly the same results by the same method, independently of the authors.   They also reported the formation of a zinc complex bearing the formula $Zn(EX)_3^-$.   In the case of the reaction of lead (II) ion with an excess of EX^-, the dissolution of lead species was also found, but the concentration of the dissolved lead species was not sufficient for the polarographic measurements.

Summary

The reduction of cadmium (II) ion in the presence of an excess of KEX was studied with the dropping mercury electrode, and emf measurement was carried out by using cadmium amalgam electrode.   The d.c. polarogram gave a well-defined wave corresponding to the two-electron reduction from cadmium (II) ion to cadmium amalgam.   Employing the polarographic method the complex obtained from EX^- and Cd (II) ion was found to be 1:4 complex anion, $Cd(EX)_4^{2-}$. From emf measurements nearly the same result was obtained without any assumption and the absence of $Cd(EX)_3^-$ was suggested.

(16)   H. Kodama and K. Hayashi, J. Electroanal, Chem., 14 (1967), 209.