BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (12), 3518—3523 (1976) [Vol. 49, No. 12

# The Polarography of the Cadmium(II)-2-Carboxy-1-pyrrolidinecarbodithioate Chelate

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(Received May 15, 1976)

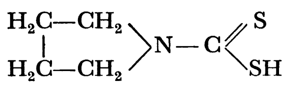
The electrochemical behavior of the cadmium(II) ion in the presence of 2-carboxy-1-pyrrolidinecarbodithioic acid ($H_2$cpcd) as a chelating agent was investigated in an alkaline medium by d.c. polarography, a.c. polarography, cyclic voltammetry, and chronopotentiometry. The cadmium(II) chelate gave a reversible two-electron reduction wave at $-0.86$ V *vs.* SCE, with a postwave at $-0.95$ V. From the dependence of the total wave height on the mercury column height and from the methods of cyclic voltammetry, the electrode reduction of the cadmium(II) chelate was found to be diffusion-controlled. The diffusion current constant was 2.42 $\mu$A mol$^{-1}$ m$^3$ mg$^{-2/3}$ s$^{1/2}$. The postwave was identified as an adsorption wave of the cadmium(II) chelate from the dependence of the postwave height on the mercury column height, the a.c. peak height, the electrocapillary curves, and the results of chronopotentiometry. The surface excess of cadmium(II) chelate adsorbed on the mercury electrode was evaluated by means of three different electrochemical techniques. The composition of the cadmium(II)-cpcd chelate in the presence of excess $H_2$cpcd was Cd(cpcd)$_2^{2-}$, and the overall stability constant was estimated to be $8.0\times10^{12}$ at 25.0 °C and $\mu=1.5$.

1-Pyrrolidinecarbodithioic acid (Hpcd) [I] is more stable to an acidic solution than 1,1-diethyldithiocarbamic acid, and it forms insoluble complexes with various metal ions. The [I] reagent has been used for the colorimetric determinations and atomic absorption spectrophotometric determinations of metal ions after solvent extraction,[1-3] X-ray analysis of the mercury complex[4] and electrochemical studies of the manganese complex.[5]

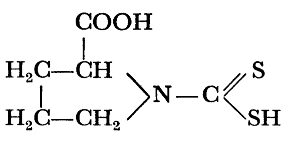
The reagent synthesized by the introduction of a carboxyl group at the 2-position of [I], 2-carboxy-1-pyrrolidinecarbdithioic acid ($H_2$cpcd)[II], has been recently found to form soluble complexes with metal ions in an aqueous solution,[6] and it may be that [II] can be used as an analytical reagent, much like other dithiocarbamic acids.

In a previous paper,[7] the polarographic behavior of [I] and [II], particularly the characteristics of the adsorption prewave, was investigated. Few of polarographic studies of the adsorption postwave has been presented than those of the prewave.[8-10] This paper will deal with the polarographic behavior of the cadmium(II) ion in the presence of $H_2$cpcd, and particularly with the characteristics of the adsorption postwave.

The structural formulas of [I] and [II] are as follows:



[I]



[II]

## Experimental

*Reagents.* Ammonium salt of [II] was prepared by the following procedure. L-Proline (11.5 g) was dissolved in a minimum amount of methanol, and then carbon disulfide (6 ml) was added. The solution was saturated with ammonia gas at 0 °C. The product was filtered off, recrystallized a few times by dissolving it in methanol and precipitating with ethyl ether, and dried under a vacuum for 24 h. Found: C, 32.07; H, 6.64; N, 18.56%. Calcd for $C_6H_{15}O_2N_3S_2$: C, 31.98; H, 6.71; N, 18.65%.

The cadmium(II) sulfate solution was standardized by chelatometric titration, with EDTA as the titrant. All chemicals were of an analytical reagent grade and were used without further purification.

*Apparatus.* The d.c. and a.c. polarograms were recorded with a Yanagimoto PA-102 polarograph connected to a conventional H-type cell, which was used in conjunction with a saturated calomel electrode (SCE) as a reference electrode and, if necessary, a coiled platinum wire electrode as a counter electrode. The dropping mercury electrode (DME) had the following characteristics: mercury flow-rate $m=0.499$ mg s$^{-1}$ and drop time $t=5.24$ s in a 0.5 mol dm$^{-3}$ sodium sulfate solution at an open circuit and at a mercury column height $h=60$ cm. The AC current was by-passed by the use of a 200 $\mu$F capacitor between the coiled platinum wire electrode and SCE. Cyclic voltammograms were recorded with Riken Denshi F-32 or F-43 X-Y recorders in conjunction with the polarograph, using a hanging mercury drop electrode (HMDE). Chronopotentiograms were also recorded with X-Y recorder in conjunction with a Riken Denshi transient time converter TCA-200 using a slow dropping mercury electrode, where $m=0.0349$ mg s$^{-1}$ and $t=208.2$ s. A constant current for the chronopotentiometric measurements was obtained using a dry cell of 200 V and appropriate resistors. The pH of a sample solution was measured with a Toa Denpa HM-5A pH meter.

*Procedure.* To a freshly prepared sample solution containing 0.5 mol dm$^{-3}$ sodium sulfate as a supporting electrolyte, a 0.02 mol dm$^{-3}$ sodium borate-sodium hydroxide buffer was added to prevent the sample from decomposition because of the poor stability of $H_2$cpcd in an acidic solution.[11] Solutions were de-aerated with highly purified nitrogen gas for 15 min before recording the polarograms. The cell was immersed in a water thermostat controlled at 25±0.1 °C, and measurements were carried out under a nitrogen atmosphere. Electrocapillary curves weer obtained by converting the drop times into the interfacial tension in the potential range from 1.0—1.8 V.

## Results and Discussion

*D.c. and a.c. Polarography.* Figure 1 shows, the d.c. and a.c. polarograms of the cadmium(II) ion in an alkaline solution containing excess $H_2$cpcd. At the concentrations of $2\times10^{-4}$ mol·dm$^{-3}$ cadmium(II) and $1\times10^{-2}$ mol dm$^{-3}$ $H_2$cpcd, the d.c. polarogram gives the main wave A at $-0.86$ V and a postwave, B,

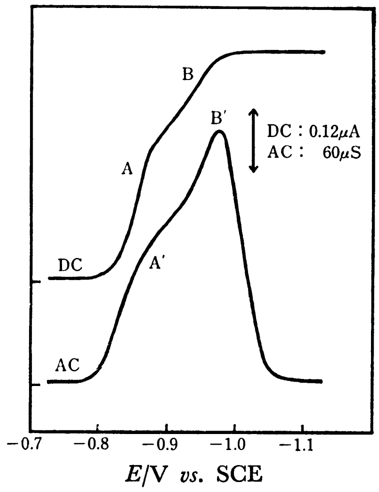


Fig. 1. Polarograms of cadmium(II)-cpcd chelate. [Cd(II)] = $2\times10^{-4}$ mol dm$^{-3}$, [cpcd] = $1\times10^{-2}$ mol dm$^{-3}$, pH 9.4.

at −0.95 V. Two peaks, A′ and B′ of the a.c. polarogram correspond to the d.c. waves. The wave heights are almost constant in the pH range from 4.5 to 11.0 and decrease below pH 4.5. The reversibility of the electrode reactions has been introduced by Senda *et al.* and the reversibility constant is expressed as $K = Y_p i_l^{-1} n^{-1} t^{-1/2}$ where $Y_p$ is the peak admittance of the a.c. wave. The $K$ values for the electrode processes of the two reduction waves are 70.4 and 439.9 S A$^{-1}$ s$^{-1/2}$ respectively. The latter value is much greater than the former, which shows a reversible process. These values suggest that the electrode reaction accompanies a specific adsorption. The adsorption of the reactant and/or product will affect the observed electrochemical behavior. Brdička has shown that, on d.c. polarography, adsorption of the product should manifest itself as an adsorption-controlled prewave, while, the adsorption of the reactant should appear as a postwave.[12)]

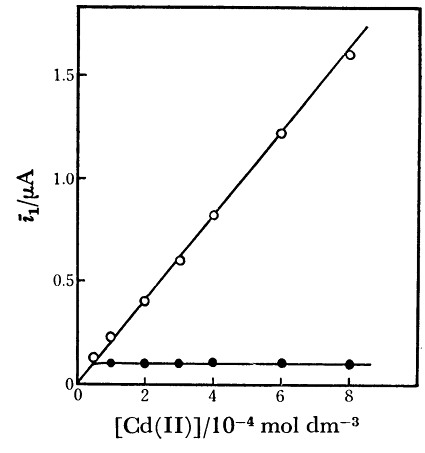


Fig. 2. Dependence of the limiting currents on the concentration of cadmium(II) ion.
[cpcd] = $1\times10^{-2}$ mol dm$^{-3}$, pH 9.4, ○: total wasve (A+B), ●: postwave(B).

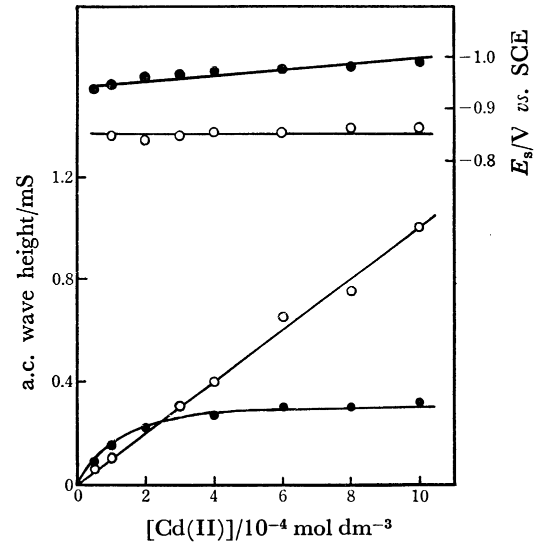


Fig. 3. Dependence of the summit potentials and a.c. wave heights on the concentration of cadmium(II) ion.
[cpcd] = $1\times10^{-2}$ mol dm$^{-3}$, pH 9.4, ○: 1st wave(A′), ●: 2nd wave(B′).

As Fig. 2 shows, the height of the B postwave is independent of the concentration of the cadmium(II) ion in the range over $1\times10^{-4}$ mol dm$^{-3}$, while that of the total wave (A+B) is proportional to the concentration in the range less than $1\times10^{-3}$ mol dm$^{-3}$. Therefore, the postwave may be considered to be an adsorption wave of the reactant. Figure 3 shows the dependence of the a.c. peak height and the summit potential on the concentration of the cadmium(II) ion. The height of the second peak, B′, increases nonlinearly with an increase in the concentration and approaches a limiting value, while that of the first peak, A′, is approximately proportional to the concentration. The summit potential of B′ shifts to a more negative potential with an increase in the concentration, while that of A′ is independent of the concentration. From these results, the second a.c. wave seems to be a tensammetric desorption wave.[13,14)]

The plot of $\log(i/(i_d - i))$ *vs.* $E$ gives a straight line with a reciprocal slope of 30 mV, although the plot displays a downward curvature near the potential corresponding to the postwave. The electrode process of the cadmium(II) chelate is found to be a reversible two-electron reduction.

*Electrocapillary Curves.* The electrocapillary curves of the cadmium(II) ion in the presence of excess $H_2$cpcd are shown in Fig. 4. In the presence of $H_2$cpcd alone a marked depression of the interfacial tension of mercury is observed in the potential range from 0 to −0.85 V. At more negative potentials than about 0.85 V, the interfacial tension of mercury in the presence of $H_2$cpcd is almost identical to that in its absence. As has been reported previously,[7)] cpcd$^{2-}$ itself adsorbs strongly on the surface of the DME in the above potential range. On the addition of the cadmium(II) ion to the $H_2$cpcd solution, the interfacial tension is depressed much more than in the presence of $H_2$cpcd only, and the potentials of the desorption shift to more negative values as the concentration of

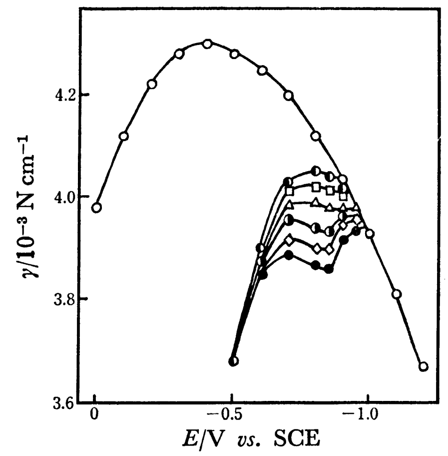


Fig. 4. Electrocapillary curves of cadmium(II)-cpcd chelate.
[cpcd] = $1\times10^{-2}$ mol dm$^{-3}$, [Cd(II)] = ◐: 0, □: $1\times10^{-5}$, △: $2\times10^{-5}$, ◑: $4\times10^{-5}$, ◇: $8\times10^{-5}$, ●: $2\times10^{-4}$ mol dm$^{-3}$, ○: base solution.

the cadmium(II) ion increases. At $2\times10^{-4}$ mol dm$^{-3}$ cadmium(II), the interfacial tension is depressed in the potential range from 0 to −0.95 V and reaches its lower limit. This behavior corresponds to the saturation of the adsorbate on the electrode surface. The potential slightly more positive than that of the desorption corresponds to be the potential of the postwave on the d.c. polarogram. Therefore, the postwave is also assigned to the adsorption wave of the cadmium(II) chelate. The minimum of the interfacial tension on the electrocapillary curves for the cadmium(II) chelate appears at the potential of −0.85 V, which corresponds to the initial rise in the polarogram.

*Effect of the Mercury Column Height.* Table 1 shows the dependence of the wave heights on the mercury column height. The limiting current of the total wave (A+B) is proprotional to $h^{1/2}$; hence, the electrode process is diffusion-controlled. According to the Ilkovič equation, the diffusion current constant, $I_d$, and the diffusion coefficient, $D$, of the cadmium chelate can be calculated: $I_d = 2.42$ μA mol$^{-1}$ m$^3$ mg$^{-2/3}$ s$^{1/2}$ and $D = 3.97\times10^{-6}$ cm$^2$ s$^{-1}$ where $n = 2$. From the equation of the mean adsorption current, $i_a$, gives below, $i_a$ should be proportional to $h$, because $m$ is proportional to $h$ and $t$ to $h^{-1}$. The limiting current of the B postwave is proportional to $h$, and the postwave is reassigned to the adsorption wave of cadmium(II) chelate.

Table 1. Dependence of the limiting currents on the mercury column height

| $h$<br>cm | $i_{\text{post}}$<br>nA | $i_{\text{total}}$<br>nA | $i_{\text{post}}/h$<br>nA·cm$^{-1}$ | $i_{\text{total}}/h^{1/2}$<br>nA·cm$^{-1/2}$ |
|---|---|---|---|---|
| 55.0 | 116 | 388 | 2.1 | 52.3 |
| 60.0 | 128 | 401 | 2.2 | 51.8 |
| 65.0 | 140 | 422 | 2.2 | 52.3 |
| 70.0 | 152 | 432 | 2.2 | 51.6 |
| 75.0 | 165 | 449 | 2.2 | 51.8 |

[Cd(II)] = $2\times10^{-4}$ mol dm$^{-3}$, [cpcd] = $1\times10^{-2}$ mol dm$^{-3}$, pH 9.4.

*Cyclic Voltammerty.* A cyclic voltammogram obtained under the same conditions is shown in Fig. 5. An exceptionally steep rise of the current is observed in the reduction step and is considered to be due to the adsorption of the cadmium(II) chelate. The peak current which is obtained by subtracting the current of the steep rise is proportional to the squareroot of the sweep rate. Consequently, the electrode process is the diffusion-controlled process acompanying the adsorption of the reactant.

*Chronopotentiometry*, Chronopotentiometry has often been used for the investigation of the adsorption of reactants.[15–17] Figure 6 shows a characteristic potential-time curve of the cadmium(II) chelat. The transition time constant, T, in chronopotentiometry has been revealed by Sand to be as follows; it is constant when the electrode process is diffusion-controlled:

$$T = \frac{i_A\tau^{1/2}}{C} = \frac{1}{2}\pi^{1/2}\,n\,F\,D^{1/2}$$

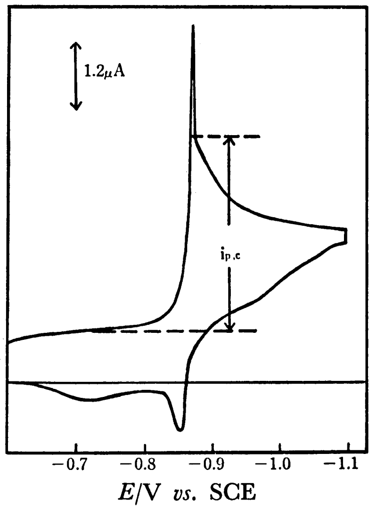


Fig. 5. Cyclic voltammogram of cadmium(II)-cpcd chelate at HMDE.
[Cd(II)] = $2\times10^{-4}$ mol dm$^{-3}$, [cpcd] = $1\times10^{-2}$ mol dm$^{-3}$, pH 9.4, sweep rate = 30 mV s$^{-1}$.

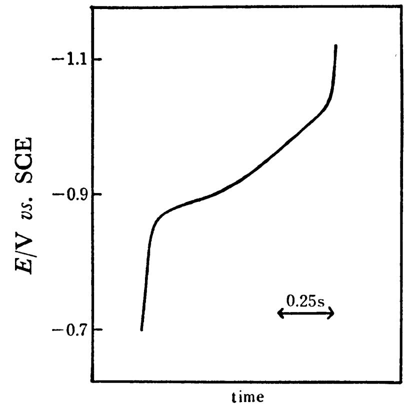


Fig. 6. Chronopotentiogram for the reduction of cadmium(II)-cpcd chelate at HMDE.
[Cd(II)] = $2\times10^{-4}$ mol dm$^{-3}$, [cpcd] = $1\times10^{-2}$ mol dm$^{-3}$, pH 9.4. $i_A = 1.66\times10^{-5}$ A cm$^{-2}$.

Table 2. Chronopotentiometric data for the reduction of $Cd(cpcd)_2^{2-}$

| $i_A$<br>$10^{-4}$ A·cm$^{-2}$ | $\tau$<br>s | $i_A\tau^{1/2}/C$<br>$10^2$ A·cm·s$^{1/2}$·mol$^{-1}$ |
|---|---|---|
| 1.01 | 1.49 | 6.16 |
| 1.19 | 1.12 | 6.31 |
| 1.46 | 0.798 | 6.52 |
| 1.85 | 0.558 | 6.91 |
| 2.57 | 0.341 | 7.50 |
| 3.78 | 0.203 | 8.52 |
| 5.32 | 0.136 | 9.82 |
| 7.68 | 0.0854 | 11.2 |

[Cd(II)] = $2\times10^{-4}$ mol dm$^{-3}$, [cpcd] = $1\times10^{-2}$ mol dm$^{-3}$, pH 9.4.

where $i_A$ is the applied current density, $\tau$ is the transition time, and F is the Faraday constant. The results for the reduction of the cadmium(II) chelate which are summarized in Table 2 show that T tends to increase with an increase in $i_A$. This behavior is indicative of the adsorption of the electroactive reactant on the surface of the mercury drop electrode.

*Surface Excess.* $\Gamma_m$ was calculated by the quantitative treatment of the limiting current caused by the formation of a monolayer of the reactant on the surface of the dropping mercury electrode.[12] Provided the quantity of electricity, $Q$, is based on the formation of a monolayer until the final time of drop-growth, $Q$ is expressed as Eq. 1:

$$Q = nFA_t\Gamma_m \tag{1}$$

Where $\Gamma_m$ is the number of moles of a monolayer in a unit area, *i.e.*, the surface excess, $A_t$ is the srea of a mercury drop after $t$ seconds, and $n$ is the number of electrons per mole of a monolayer. Therefore, the net current until the final time of drop-growth is given as:

$$i_a = \frac{\partial Q}{\partial t} = nF\Gamma_m\left(\frac{\partial A_t}{\partial t}\right) \tag{2}$$

Provided a mercury drop is a complete sphere, the following equation is given:

$$A_t = \left(\frac{3mt}{4\pi d}\right)^{2/3} = 0.848\, m^{2/3}t^{2/3} \tag{3}$$

where $m$ is expressed in g s$^{-1}$ and where $d$ is the density of mercury (13.6 g cm$^{-3}$). The net current introduced from Eq. 2 is:

$$i_a = 5.47\times10^4\, n\, m^{2/3}t^{-1/3}\Gamma_m \tag{4}$$

and from Eq. 4 the mean adsorption current is:

$$\bar{i}_a = \frac{1}{t_m}\int_0^{t_m} i_a\,dt = 8.17\times10^8\, n\, m^{2/3}t_m^{-1/3}\Gamma m \tag{5}$$

where $m$ is expressed in mg s$^{-1}$ and $\bar{i}_a$ in μA.

The surface excess of the cadmium(II) chelate can be calculated by the following three methods. The first method[12] is based upon the mean adsorption current of the d.c. polarogram, using Eq. 5. On substituting 0.114 μA for $\bar{i}_a$, $\Gamma_m$ is $1.93\times10^{-10}$ mol cm$^{-2}$.

The area occupied by one molecule of an adsorption monolayer can be calculated as follows. The maximum area of a mercury drop, $A_m$ is obtained by the substitution of $t$ for $t_m$ in Eq. 3. $\bar{i}_a t_m/A_m$ is the quantity of electricity per area at the last moment of drop-growth. The quantity of electricity required to form a monolayer according to a two-electron process is:

$$\frac{nF}{\text{Avogadro number}} = 3.20\times10^{-19}\ \text{C molecule}^{-1}$$

Therefore, the area per molecule of a monolayer, $A$, is obtained by means of the following equation:

$$\bar{A} = \frac{3.20\times10^{-19}A_m}{\bar{i}_a t_m}$$

$\bar{A}$ is $85.8\times10^{-16}$ cm$^2$ molecule$^{-1}$.

The second method is a calcualtion from the interfacial tensions at the constant potential, $E$, using the following equations:[18]

$$\Gamma_s = -\frac{1}{R\Gamma}\left(\frac{\partial\gamma}{\partial \ln C}\right)_E \tag{6}$$

where $\gamma$ is the interfacial tension. Figure 7 shows the variation in the $\gamma$ of the electrocapillary curves with the concentration of cadmium(II) ion at the potential, $E$. $\Gamma_s$ is calculated to be $2.15\times10^{-10}$ mol cm$^{-2}$.

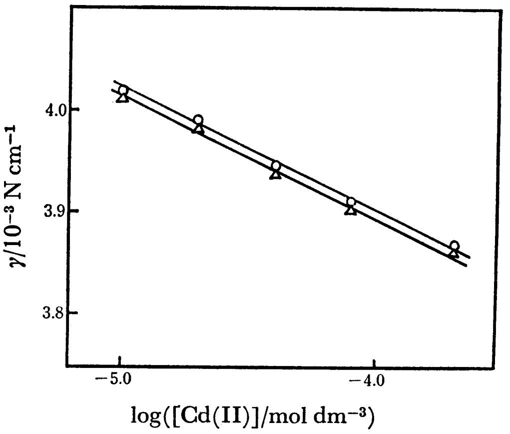


Fig. 7. Dependence of the interfacial tention on the concentration of cadmium(II) ion.
$E$ ○: −0.80 V, △: −0.85 V.

The third methcd is a calculation from the variation in $i_A\tau^{1/2}/C$ with the $\tau$ through chronopotentiometry, using various theoretical models of adsorption. Lorenz[19] proposed four theoretical models for chronopotentiomety involving the adsorption of electroactive species. These can be denoted as the ARSR, SAR, SRAR, and equilibrium cases.[17,20] The ARSR model assumes that the adsorbed reactant, AR, is coulometrically depleted prior to the reduction of the solution reactant, SR, and that $\tau$ is the sum of the transition times of the AR and SR species. The mathematical relation is:

$$i_A\tau = nF\Gamma_c + \frac{\pi D(nFC)^2}{4i_A} \tag{7}$$

The SAR model assumes that the SR and AR species react and are depleted simultaneously, that a fixed fraction of the applied current goes to each phase during the entire electrolysis, and that the relation is:

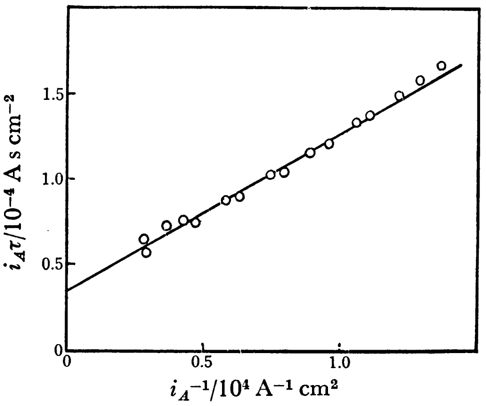


Fig. 8. The plot of $i_A\tau$ vs. $i_A^{-1}$.

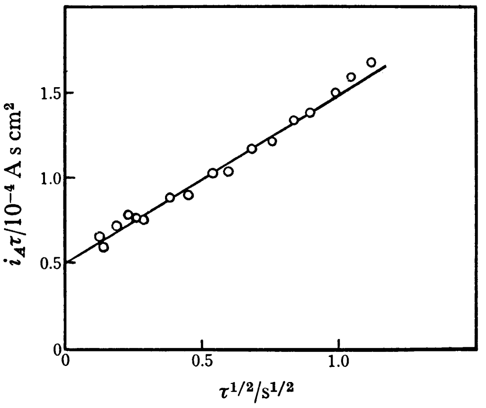


Fig. 9. The plot of $i_A\tau$ vs. $\tau^{1/2}$.

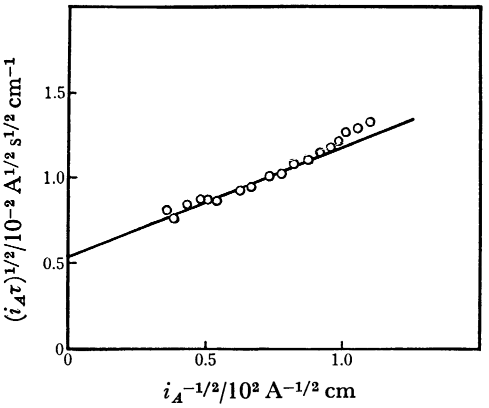


Fig. 10. The plot of $(i_A\tau)^{1/2}$ vs. $i_A^{-1/2}$.

$$i_A\tau = nF\Gamma_c + \frac{nFC(\pi D\tau)^{1/2}}{2} \tag{8}$$

The SRAR model is the reverse of the ARSR model and assumes that the SR species is coulometrically depleted prior to the reduction of the AR species and that the relation is:

$$(i_A\tau)^{1/2} = (nF\Gamma_c)^{1/2} + \frac{nFC(\pi D)^{1/2}}{2i_A^{1/2}} \tag{9}$$

The equlibrium model assumes that the species are coupled by a rapid equilibration process accroding to a linear adsorption isotherm, that they are simultaneously depleted at the total transition time, and that the relation is:

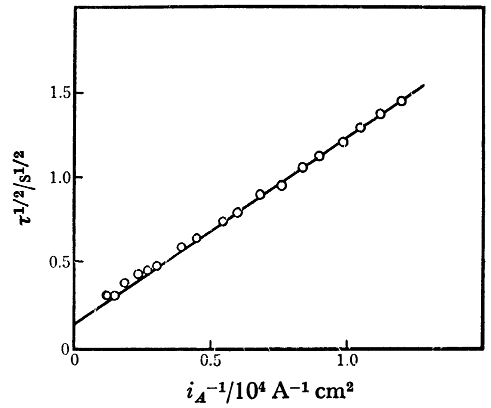


Fig. 11. The plot of $\tau^{1/2}$ vs. $i_A^{-1}$.

$$\tau^{1/2} = \frac{nFC(\pi D)^{1/2}}{2i_A} + \frac{\pi^{1/2}\Gamma_c}{2D^{1/2}C} \tag{10}$$

Figures 8 to 11 show the plots of the four models. Each of them gives a straight line, and the diffusion coefficient, $D$, can be obtained from the intercept, and $\Gamma_c$ from the slope; those values are summarized in Table 3. Although it is not possible to make a clear choice between the models on the basis of only these results, the adsorption behavior may be an equilibrium case because of the excellent linearity of the plot according to Eq. 10.

The values of the surface excess obtained from the three methods closely agree with one another. The area per molecule of a monolayer of the complex is about $80\times10^{-16}$ cm$^2$. The surface excess of Cd(cpcd)$_2^{2-}$ is shown in Table 4, together with Hg(cpcd)$_2^{2-}$ and Hg(pcd)$_2$, which are the oxidationproducts at the DME. On applying either method, the order of the magnitude of the surface excess on the mercury drop is Hg(pcd)$_2$>Hg(cpcd)$_2^{2-}$>Cd(cpcd)$_2^{2-}$. This order may be due to the steric hindrance of the carboxyl group and the spcific interaction between the mercury and the sulfur atoms.

*Effect of the Ligand Concentration.* By means of the variation in the concentration of H$_2$cpcd in the presence of the cadmium (II) ion, the stability constants of the

TABLE 3. SURFACE EXCESS AND DIFFUSION COEFFICIENT OBTAINED BY FOUR THEORETICAL MODELS FOR CHRONOPOTENTIOMETRY

| Model | $\Gamma/10^{-10}$ mol cm$^{-2}$ | $D/10^{-6}$ cm$^2$ s$^{-1}$ |
|---|---|---|
| ARSR | 2.60 | 8.16 |
| SAR | 1.84 | 6.96 |
| SRAR | 1.59 | 3.36 |
| Equilibrium | 1.10 | 9.86 |

TABLE 4. SURFACE EXCESS OF CARBODITHIOATES

| Substance | $\Gamma/10^{-10}$ mol cm$^{-2}$ | | | Reference |
|---|---|---|---|---|
| Cd(cpcd)$_2^{2-}$ | 1.9[a] | 2.1[b] | 1.1[c] | this work |
| Hg(cpcd)$_2^{2-}$ | 4.8 | 2.6 | — | Ref. 7 |
| Hg(pcd)$_2$ | 6.9 | 5.8 | — | Ref. 7 |

a) D.c. polarography. b) Electrocapillary curve.
c) Chronopotentiometry.

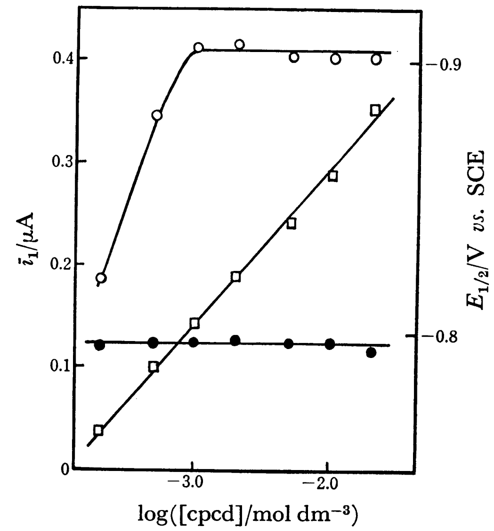


Fig. 12. Dependence of the limiting currents and the halfwave potential on the ligand concetration. [Cd(II)]$=2\times10^{-4}$ mol dm$^{-3}$. ○: total wave(A+B), ●: postwave(B), □: $E_{1/2}$ of the main wave.

cadmium (II)-cpcd chelate can be determined. Figure 12 shows the dependence of these wave heithts and half-wave potentials on the concentartion of $H_2$cpcd. The limiting current of the total wave (A+B) is nearly constant in concentrations more than $10^{-3}$ mol dm$^{-3}$. That of the postwave B is independent of the concentration. The half-wave potential of the main wave, A, shifts linearly to a more negative potential as the concentration of the ligand increases. The slope of the $E_1/_2$ vs. log[cpcd]plot is 57 mV, which corresponds the formation of the 1 : 2 complex. The overall stability costant of the chelate, $\beta_2$, is calculated by the Lingane method[21]; it is $5.1\times10^{12}$ at 25 °C and $\mu=$ 1.5. The relationship between $E_{1/2}$ and the ligand concentration can slao be analyzed by the method of DeFord and Hume[22]; the value of $\beta_1$ and $\beta_2$ are $5.5\times10^8$ and $8.0\times10^{12}$ respectively.

The electrode reactions for the cadmium(II) chelate are inferred to proceed according to the following four steps:

(1) The Cd(cpcd)$_2^{2-}$ reactant diffuses toward the DME, and then the reactant is completely adsorbed on the surface. The adsorbed molecules are stabilized because of the adsorption energy; hence, the reduction of the adsorbed reactant require a much higher enregy than that of the solute reactant.

$$\mathrm{Cd(cpcd)_2^{2-}} \rightleftharpoons \mathrm{Cd(cdcd)_2{}^{2-}{}_{ads.}}$$

(2) The Cd(cpcd)$_2^{2-}$ species, which diffuses from the bulk of the solution, is reduced at first.

$$\mathrm{Cd(cpcd)_2^{2-}} + 2e \rightleftharpoons \mathrm{Cd(Hg)} + 2\,\mathrm{cpcd^{2-}} \quad \text{(main wave)}$$

(3) The reduction of Cd(cpcd)$_2{}^{2-}{}_{ads.}$, which was stabilized by adsorption, requires a high energy, and then the wave appears at amore negative potential.

(4) The Cd(cpcd)$_2^{2-}$, which diffuses from the bulk of the solution, is directly reduced.

The authors wish to thank Mr. A. Ichimura for his valuable suggestions and discussions in the course of this work.

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