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Polarography of Halides in Dimethylformamide. III. The Chloride Ion, the Trichloromercurate Ion, and Mercuric Chloride

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The polarographic behavior of the chloride ion at the dropping mercury electrode was investigated in dimethylformamide. The chloride ion gives two diffusion-controlled anodic waves. On the basis of the analysis of the waves, the first anodic wave can be ascribed to the reversible oxidation of mercury to form either the tri- or the tetrachloromercurate ion. At the more negative part of the potential in the wave, where the concentration of the chloride ion on the mercury drop is much higher than that of the mercuric ion dissolved, the higher complex species, *i.e.*, the tetrachloromercurate ion, is the main product of the electrode reaction. As the potential of the dropping electrode shifts toward less negative potentials, the concentration of the chloride ion at the electrode surface decreases more and more and the formation of the trichloromercurate ion becomes predominant. When a constant diffusion current is attained, only the trichloromercurate ion is formed and the formation of the tetrachloromercurate ion can be neglected. On the other hand, the second anodic wave can be ascribed to the reversible oxidation of mercury to mercuric chloride.

The polarographic behavior of the bromide ion, the iodide ion, and their mercuric complexes in dimethylformamide (DMF) have been reported on in previous papers.[1,2] It has been shown that each of the bromide and iodide ions gives two anodic waves; the first wave corresponds to the reversible oxidation of mercury to the trihalogenomercurate ion (HgX_3^-), and the second wave, to the reversible oxidation of mercury to mercuric halide (HgX_2).

The present investigation will deal with the mechanism of the electrode reaction of the chloride ion, the trichloromercurate ion, and mercuric chloride at the dropping mercury electrode in DMF.

Experimental

The methods of the purification of DMF and mercuric chloride and of the preparation of tetraethylammonium perchlorate and tetraethylammonium chloride were described in the previous papers.[1,2] A stock solution of tetraethylammonium trichloromercurate in DMF was prepared by adding equimolecular amounts of tetraethylammonium chloride and mercuric chloride to DMF.

The polarographic cell and the dropping mercury electrode were the same as those described previously.[1,2] D.c. polarography, controlled potential electrolysis, and conductivity measurements were carried out according to the same procedures as were used before. Likewise, all the potentials reported in the present paper refer to the aqueous saturated calomel electrode connected with the test solution by a DMF-agar salt bridge.[3]

Results and Discussion

Complex Formation between Tetraethylammonium Chloride and Mercuric Chloride in DMF. The composition of the complex ion between the chloride ion and mercuric chloride was examined in DMF by means of conductometric titration. As the previous papers showed,[1,2] information concerning the complex formation between the halide ion and the mercuric ion helps us to elucidate the mechanism of the electrode reaction of the halide ion at the dropping mercury electrode. The results are given in Fig. 1. As mercuric chloride was added to a solution of tetraethylammonium chloride in DMF, the specific conductance of the solution decreased. It attained its minimum value when the mole ratio of mercuric chloride to tetraethylammonium chloride became equal to about 0.6. This suggests that complex formation occurs in solution and that the resulting complex ion is the tetrachloromercurate ion ($HgCl_4^{2-}$). The addition of more mercuric chloride increased the specific conductance, which reached virtually a constant value when the mole ratio became equal to unity. This indicates that

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1) Y. Matsui, R. Kawakado and Y. Date, This Bulletin, **41**, 2913 (1968).

2) Y. Matsui, Y. Kurosaki and Y. Date, *ibid.*, **43**, 1707 (1970).

3) K. Takaoka, *Rev. Polarography*, **14**, 63 (1966).

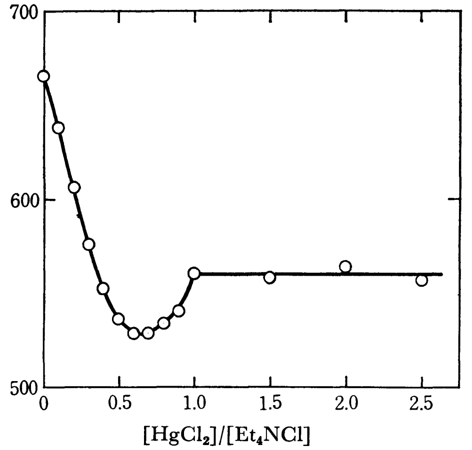

Fig. 1. Effect of $HgCl_2$ on the specific conductance of 10 mM of Et_4NCl in DMF at 25°C.

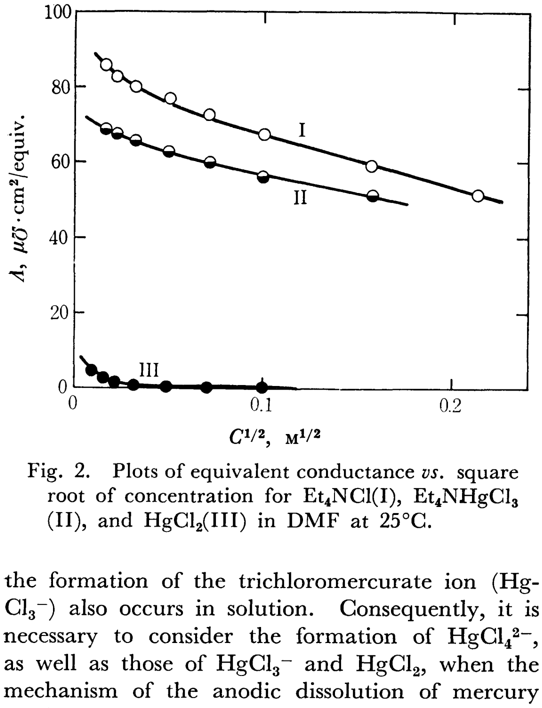

Fig. 2. Plots of equivalent conductance *vs.* square root of concentration for Et_4NCl(I), Et_4NHgCl_3 (II), and $HgCl_2$(III) in DMF at 25°C.

the formation of the trichloromercurate ion ($HgCl_3^-$) also occurs in solution. Consequently, it is necessary to consider the formation of $HgCl_4^{2-}$, as well as those of $HgCl_3^-$ and $HgCl_2$, when the mechanism of the anodic dissolution of mercury in the presence of the chloride ion is studied in DMF.

The equivalent conductances of a few connected salts are plotted as a function of the square root of the concentration in Fig. 2. The results for tetraethylammonium chloride and tetraethylammonium trichloromercurate approximately fit the Onsager equation, indicating that these salts behave as strong electrolytes in DMF. The equivalent conductance of mercuric chloride is very low, however, and its plotting does not fit the Onsager equation, which shows that the chloride is a weak electrolyte in this medium.

D.C. Palarography. Figure 3 shows the d.c. polarograms of tetraethylammonium chloride(**I**), mercuric chloride(**III**), and their equimolar mixture, *i.e.*, tetraethylammonium trichloromercurate (**II**) in DMF containing 0.1 M tetraethylammonium perchlorate and 0.005% polyvinyl chloride (PVC), which was added to suppress the maximum arising on the cathodic wave of tetraethylammonium trichloromercurate or on the second cathodic wave

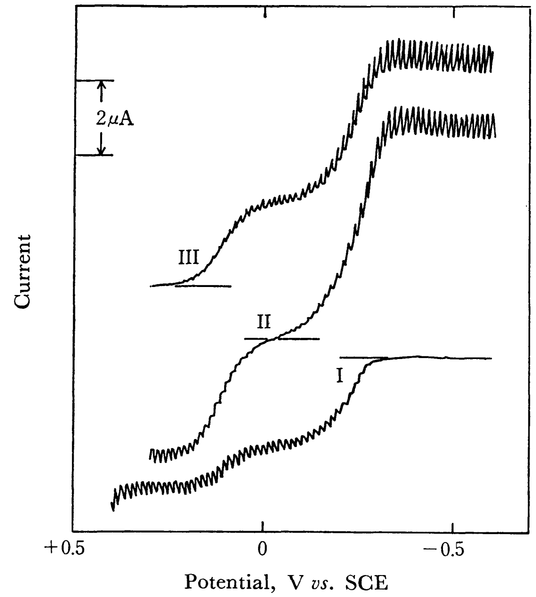

Fig. 3. Polarograms of 1.0 mM solutions of Et_4NCl (I), Et_4NHgCl_3(II), and $HgCl_2$(III) in DMF containing 0.1 M Et_4NClO_4 and 0.005% PVC at 25°C.

TABLE 1. POLAROGRAPHIC CHARACTERISTICS AT VARIOUS CONCENTRATIONS

Depolarizer	Concn. (mM)	$E_{1/2}$ (V *vs.* SCE) more pos.	$E_{1/2}$ (V *vs.* SCE) more neg.	I_d more pos.	I_d more neg.
Et_4NCl	0.10	+0.122	−0.136	0.59	0.94
	0.25	+0.121	−0.152	0.54	1.08
	0.50	+0.131	−0.165	0.56	1.25
	1.00	+0.131	−0.190	0.50	1.20
	2.50	+0.160	−0.213	0.51	1.24
	5.00	+0.175	−0.233	0.55	1.25
Et_4NHgCl_3	0.10	+0.110	−0.153	1.37	2.98
	0.25	+0.127	−0.179	1.51	3.15
	0.50	+0.142	−0.189	1.37	2.93
	1.00	+0.157	−0.209	1.46	2.95
	2.50	+0.173	−0.242	1.49	2.87
$HgCl_2$	0.10	+0.112	−0.164	1.14	2.38
	0.25	+0.113	−0.177	0.79	2.05
	0.50	+0.127	−0.188	0.83	2.12
	1.00	+0.140	−0.216	0.89	2.06
	2.50	+0.151	−0.234	1.10	2.06

TABLE 2. RELATION BETWEEN LIMITING CURRENTS OF 0.50 mM OF DEPOLARIZERS AND EFFECTIVE HEADS OF THE DROPPING MERCURY ELECTRODE

Depolarizer	$h_{corr.}$ (cm)	i_d, (μA) more pos.	i_d, (μA) more neg.	$i_d/(h_{corr.})^{1/2}$ more pos.	$i_d/(h_{corr.})^{1/2}$ more neg.
Et_4NCl	37.2	0.31	0.80	0.051	0.131
	43.2	0.33	0.85	0.050	0.129
	53.2	0.37	0.95	0.051	0.130
	63.2	0.38	1.01	0.048	0.127
	73.2	0.42	1.10	0.049	0.129
	82.2	0.43	1.15	0.048	0.128
Et_4NHgCl_3	37.2	0.94	2.03	0.154	0.333
	43.2	1.00	2.17	0.152	0.330
	53.2	1.12	2.40	0.154	0.330
	63.2	1.18	2.60	0.148	0.328
	73.2	1.25	2.80	0.146	0.328
	82.2	1.32	2.96	0.146	0.328
$HgCl_2$	37.2	0.53	1.30	0.087	0.213
	43.2	0.60	1.45	0.091	0.220
	53.2	0.66	1.60	0.091	0.220
	63.2	0.74	1.75	0.093	0.220
	73.2	0.79	1.88	0.092	0.220
	82.2	0.84	2.06	0.093	0.226

of mercuric chloride. The polarographic characteristics of these depolarizers at various concentrations are given in Table 1. The relation between the limiting currents and the effective heads of the dropping mercury is given in Table 2. As is shown in these tables, all the limiting currents are virtually proportional to the bulk concentrations of the corresponding depolarizers and also to the square root of the effective pressure on the mercury drop, indicating that all these waves are diffusion-controlled.

It might be considered that the mechanism of the electrolytic oxidation of mercury in the presence of the chloride ion is essentially identical with that in the presence of the bromide or iodide ion, and that it may be expressed as follows:

$$2Hg + 6Cl^- \rightleftarrows 2HgCl_3^- + 4e \qquad (1)$$

$$Hg + 2HgCl_3^- \rightleftarrows 3HgCl_2 + 2e \qquad (2)$$

In fact, some of the results can indeed be explained in terms of this mechanism: (1) The chloride ion gives two anodic waves, the trichloromercurate ion, two waves and anodic, cathodic, and mercuric chloride, two cathodic waves, all within the same potential region. (2) The height of the wave occurring at the more negative potential is approximately equal to twice that of the wave occurring at the more positive potential in each depolarizer.

This mechanism is also suggested by the results of the large-scale electrolysis of mercuric chloride with a controlled potential. When mercuric chloride was reduced at the potential (−0.04 V *vs.* SCE) of the plateau of the first cathodic wave, using a Hg pool cathode and a Pt plate anode, the quantity of electricity transfered per mole of the depolarizer (n) was equal to 0.77 $\boldsymbol{F}$ (calculated for Eq. (1); 0.67 $\boldsymbol{F}$); moreover, the d.c. polarogram of the catholyte agreed well with that of the trichloromercurate ion. The electroreduction of mercuric chloride at the potential (−0.62 V *vs.* SCE) of the plateau of the second cathodic wave yielded the chloride ion, the formation of which was confirmed by the d.c. polarogram of the catholyte. The value of n was equal to 2.00 $\boldsymbol{F}$ (calculated for Eqs. (1) and (2): 2.00 $\boldsymbol{F}$).

This mechanism, however, overlooks the formation of the tetrachloromercurate ion, which is clearly indicated by the conductometric titration described above. It was immediately ascertained by analyzing the d.c. polarograms of the chloride ion, that the formation of the tetrachloromercurate ion as well as that of the trichloromercurate ion must be considered. If the electrode reaction is expressed by Eqs. (1) and (2), the potential of the dropping mercury electrode is given for the first anodic wave of the chloride ion by:1)

$$E_n = C_n + (\boldsymbol{R}T/2\boldsymbol{F})\ln\{i/(i_d-i)^3\} \qquad (3)$$

and for the second anodic wave by:

$$E_p = C_p + (\boldsymbol{R}T/2\boldsymbol{F})\ln\{i^3/(i_d-i)^2\} \qquad (4)$$

The results of the analysis of the waves are given in Fig. 4. The plot of $\log\{i^3/(i_d-i)^2\}$ against the potential for the second anodic wave gives a fairly good straight line, with a slope equal to 0.029 V (calculated for Eq. (4): 0.030 V), indicating that Eq. (2) is valid. On the other hand, the plot of $\log\{i/(i_d-i)^3\}$ against the potential for the first anodic wave became considerably curved on the less negative side. Furthermore, the slope of the

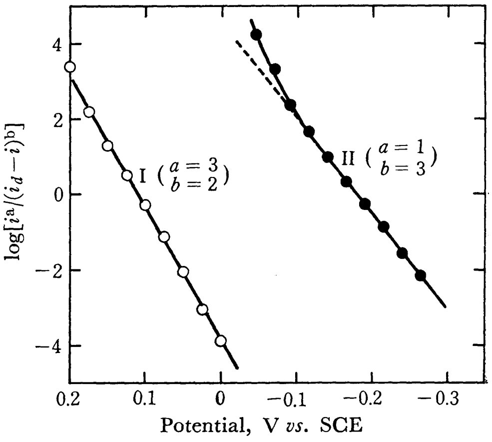

Fig. 4. Log plots for the waves of Et_4NCl.
Reciprocal slope: I, 0.029 V; II, 0.038 V

log plot (0.038 V) was somewhat greater than that expected from Eq. (3) (0.030 V).

Similar results have been reported by Given and Peover[4] in the polarographic study of lithium chloride in DMF. They assumed that the first anodic wave of the chloride ion was due to the reversible oxidation of mercury to the tetrachloromercurate ion, and they plotted log $\{i/(i_d-i)^4\}$ against the potential of the dropping mercury electrode. Their plot, however, became curved at the less negative values of the potential. They attributed the deviation of the plot to the dissociation of the tetrachloromercurate ion into the trichloromercurate ion and the chloride ion.

On the basis of these facts, we considered that the first anodic wave of the chloride ion cannot simply be ascribed to the electrochemical equilibrium expressed by Eq. (1). The tetrachloromercurate ion rather than the trichloromercurate ion is supposed to be mainly formed at the more negative part of the potential in the wave (Eqs. (5) and (6)), for here the concentration of the chloride ion on the mercury drop is much higher than that of the mercuric ion dissolved.

$$\mathrm{Hg} \rightleftarrows \mathrm{Hg^{2+}} + 2\mathrm{e} \tag{5}$$

$$\mathrm{Hg^{2+}} + 4\mathrm{Cl^-} \rightleftarrows \mathrm{HgCl_4{}^{2-}} \tag{6}$$

As the potential becomes more positive, the concentration of the mercuric ion dissolved may increase more and more and the formation of the trichloromercurate ion may become predominant (Eq. (7)):

$$\mathrm{Hg^{2+}} + 3\mathrm{Cl^-} \rightleftarrows \mathrm{HgCl_3{}^-} \tag{7}$$

Conversely, when the trichloromercurate ion is electrolytically reduced, the tetrachloromercurate ion as well as the chloride ion may be formed at the less negative part of the potential in the cathodic wave (Eqs. (8) and (9)). Since the concentration of the trichloromercurate ion on the electrode surface may decrease with an increase in the negative potential, the formation of the tetrachloromercurate ion may be suppressed at the more negative part of the potential in the wave and the trichloromercurate ion may eventually be reduced to mercury and the chloride ion:

$$\mathrm{HgCl_3{}^-} + 2\mathrm{e} \rightleftarrows \mathrm{Hg} + 3\mathrm{Cl^-} \tag{8}$$

$$\mathrm{HgCl_3{}^-} + \mathrm{Cl^-} \rightleftarrows \mathrm{HgCl_4{}^{2-}} \tag{9}$$

On the other hand, no data were obtained which are in conflict with the attribution of the second anodic wave of the chloride ion, as well as the anodic wave of the trichloromercurate ion and the first cathodic wave of mercuric chloride, to the electrochemical equilibrium expressed by Eq. (2).

The Equation of the More Negative Wave. If the mechanism of the anodic dissolution of mercury in the presence of $\mathrm{Cl^-}$ is expressed by Eqs. (5), (6), and (7), the potential at any point on the polarographic wave is given by:[5]

$$\begin{aligned} E &= C + (\boldsymbol{RT}/2\boldsymbol{F}) \ln x_0 \\ &= C' + (\boldsymbol{RT}/2\boldsymbol{F}) \ln(x_3/x_1{}^3) \\ &= C'' + (\boldsymbol{RT}/2\boldsymbol{F}) \ln(x_4/x_1{}^4) \end{aligned} \tag{10}$$

where C, C', and C'' are constant and where x_0, x_1, x_3, and x_4 are the concentrations of the simple mercuric ion, the chloride ion, the trichloromercurate ion, and the tetrachloromercurate ion respectively at the electrode surface.

Provided that a steady state is reached very quickly as the applied potential is changed, the current at any point of the wave should be equal to the sum of the rates of diffusion of the mercuric complexes formed by electrolysis. As Heyrovsky and Ilkovic[6] described, the rate of diffusion can be assumed to be directly proportional to the difference in concentration between the electrode surface and the bulk of the solution. Hence, the current should be given by:

$$i = k_3x_3 + k_4x_4 \tag{11}$$

where k_3 and k_4 are the proportionality constants of the tri- and tetrachloromercurate ions respectively, as defined by the Ilkovic equation. Likewise, the amount of the chloride ion diffusing up to the electrode surface in a unit of time should be euqal to that diffusing off from the electrode surface in the form of mercuric complexes. Hence, we obtain:

$$k_1'({}^*x_1 - x_1) = 3k_3x_3 + 4k_4x_4 \tag{12}$$

where k_1' is the proportionality constant of the chloride ion and where ${}^*x_1$ is the constant concentration of the chloride ion in the bulk of the solution. The concentrations of the chloride and tetrachloromercurate ions at the electrode surface, x_1 and x_4, decrease with an increase in the anodic current of the wave, with the result that these ions are consumed for the reactions with the dissolved mercuric ion, thus forming the trichloromercurate ion. When a constant diffusion current, i_d, is attained, both x_1 and x_4 have decreased to negligibly small values. Hence, we have:

$$k_1'{}^*x_1 = 3i_d \tag{13}$$

Eq. (13) shows that the value of k_1' is equal to three times that of the Ilkovic equation constant for the chloride ion (k_1).

By introducing Eq. (13) into Eq. (12), we obtain:

$$3i_d - k_1'x_1 = 3k_3x_3 + 4k_4x_4 \tag{14}$$

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[4] P. H. Given and M. E. Peover, *J. Chem. Soc.*, **1959**, 1602.

[5] Since the concentrations of the species concerned are very low, we took their activity coefficients as constant for the sake of simplicity.

[6] J. Heyrovsky and D. Ilkovic, *Collect. Czech. Chem. Commun.*, **7**, 198 (1935).

Since x_4 is expressed by:

$$x_4 = K_4 x_1 x_3 \tag{15}$$

where K_4 is the stepwise stability constant of the tetrachloromercurate ion, we obtain three equations for x_1, x_3, and x_4; these equations are solved as follows:

$$x_1 = (k_3/2k_1')[y - r + \{(y+r)^2 + 4ir/k_3\}^{1/2}] \tag{16}$$

$$x_3 = (1/2)[-y - r + \{(y+r)^2 + 4ir/k_3\}^{1/2}] \tag{17}$$

$$x_4 = (k_3/2k_4)[(3i_d + 2i)/k_3 + r - \{(y+r)^2 + 4ir/k_3\}^{1/2}] \tag{18}$$

where:

$$y = (3i_d - 4i)/k_3 \tag{19}$$

$$r = k_1'/k_4 K_4 \tag{20}$$

Since k_3 can be evaluated from the polarographic data, the value of y can be obtained at any point of the wave. On the other hand, the value of r is unknown; therefore, neither x_1 nor x_3 can be evaluated. However, when the plot of the potential against $\ln(x_3/x_1^3)$ calculated for an arbitrary value of r becomes linear, and when the reciprocal slope is equal to $\boldsymbol{R}T/2\boldsymbol{F}$, as is expressed by Eq. (10), the value of r must be the correct one.

Thus, as Fig. 5 shows, the linearity of the plot calculated for $r = 5\times10^{-4}$ M became better than that calculated for $r = \infty$ ($K_4 = 0$) and the reciprocal slope of the former (0.030 V) was in agreement with the theoretical value. In this treatment, the values of k_1' and k_3 were taken as equal to 6.63×10^{-3} and 5.28×10^{-3} A/M respectively.

The values of x_1, x_3, and x_4 calculated for $r = 5\times10^{-4}$ M changed with the potential of the dropping mercury electrode, as is shown in Fig. 6; the figure also clearly shows the mechanism of the electro-oxidation of mercury in the presence of the chloride ion. Thus, the tetrachloromercurate ion is formed in larger quantities than the trichloromercurate ion at potentials more negative than −0.180 V *vs.* SCE. With a decrease in the negative potential, the formation of the trichloromercurate ion becomes predominant. When a constant diffusion current is attained, only the trichloromercurate ion is formed and the formation of the tetrachloromercurate ion can be neglected.

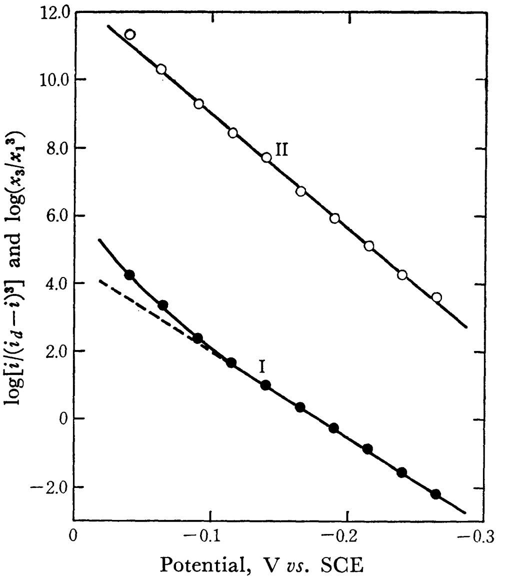

Fig. 5. Plots of $\log[i/(i_d-i)^3]$ (I) and $\log(x_3/x_1^3)$ (II) *vs.* potential for the more negative wave of Et_4NCl.

Now that the values of r and k_1' have been determined, the stepwise stability constant, K_4, of the tetrachloromercurate ion can be estimated from Eq. (20) if the value of the proportionality constant, k_4, of the tetrachloromercurate ion, as defined

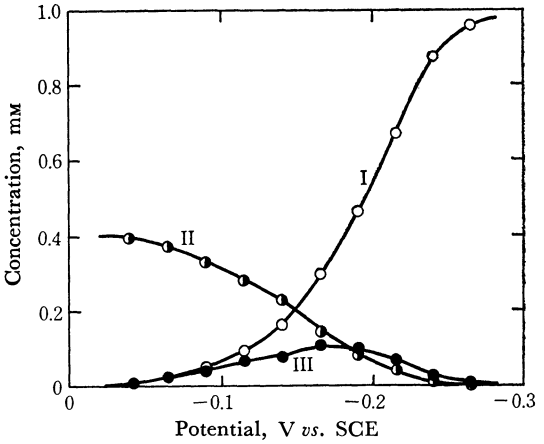

Fig. 6. Plots of the calculated concentrations of Cl^-(I), $HgCl_3^-$(II), and $HgCl_4^{2-}$(III) on the electrode surface *vs.* potential.

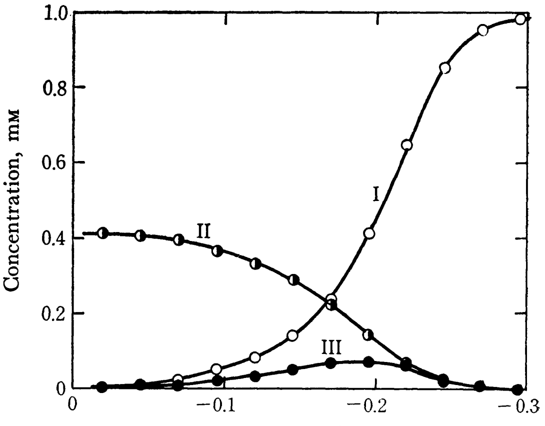

Fig. 7. Plots of the calculated concentrations of Br^-(I), $HgBr_3^-$(II), and $HgBr_4^{2-}$(III) on the electrode surface *vs.* potential.

by the Ilkovic equation, is determined. However, the value of k_4 could not be determined, because we could found no condition under which only the tetrachloromercurate ion exists as a depolarizer in the DMF solution. Assuming that k_4 is approximately equal to k_3, we can roughly estimate the value of K_4 to be $2.5\times10^3\ \text{M}^{-1}$.

In the previous papers dealing with the polarographic behavior of the bromide ion[1] and the iodide ion,[2] the formation of the tetrahalogenomercurate ion was not considered. Indeed, it might not be necessary to consider the formation of the tetraiodomercurate ion, because the plot of log $\{i/(i_d-i)^3\}$ *vs.* the potential of the dropping mercury electrode for the first anodic wave of the iodide ion yielded a straight line of the reciprocal slope equal to 0.030 V; this is in agreement with the theoretical value obtained on the basis of the formation of the triiodomercurate ion alone. However, the reciprocal slope of such a plot for the first anodic wave of the bromide ion was equal to 0.035 V, somewhat greater than the theoretical value. Since the oxidation process was proved to be reversible, this increase in the reciprocal slope indicates that the formation of the tetrabromomercurate ion may simultaneously take place. The same method of analyzing the wave as was used for the wave of the chloride ion was applied to the first anodic wave of the bromide ion; the value of r was thus estimated to be $1\times10^{-3}\ \text{M}$ ($K_4=1.3\times10^3\ \text{M}^{-1}$). Figure 7 shows the change in x_1, x_3, and x_4 with the potential of the dropping mercury electrode. It is apparent that the tetrabromomercurate ion is also formed in an appreciable quantity. In the case of the wave of the iodide ion, the plot of the potential against log (x_3/x_1^3) calculated for the r value of $1\times10^{-2}\ \text{M}$ became linear and the reciprocal slope was equal to 0.0295 V, indicating that the value of K_4 for the tetraiodomercurate ion is no more than $1.3\times10^2\ \text{M}^{-1}$.

Accordingly, it can be said that the tetrahalogenomercurate ion is always formed at the first anodic wave of any halide ion. However, the value of the K_4 of the tetraiodomercurate ion is so small that it is not necessary to consider the formation of this complex ion in the anodic dissolution of mercury in the presence of the iodide ion. On the other hand, the K_4 values of the tetrabromo- and tetrachloromercurate ions are so large that the formation of these complex ions cannot be neglected when either the bromide ion or the chloride ion is a depolarizer.