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Polarography of Halides in Dimethylformamide. II. The Iodide Ion, the Triiodomercurate Ion, and Mercuric Iodide

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The polarographic behavior of the iodide ion, the triiodomercurate ion, and mercuric iodide at the dropping mercury electrode was investigated in dimethylformamide, using d.c. polarography, controlled potential electrolysis, and oscillographic polarography with a multi-triangular voltage sweep. The iodide ion gives two well-defined anodic waves: the first wave corresponds to the reversible oxidation of mercury to the triiodomercurate ion, and the second, to the reversible oxidation of mercury to mercuric iodide. A maximum arises on the reduction wave of the triiodomercurate ion, but it is suppressed by the addition of a small amount of polyvinyl chloride. The oscillographic polarograms and electrocapillary curves suggested that the iodide ion, like the triiodomercurate ion and mercuric iodide, is strongly adsorbed on the dropping mercury electrode. The maximum on the wave due to the reduction of the triiodomercurate ion to mercury and the iodide ion was ascribed to the convection of the mercury drop, which was itself probably caused by the abrupt desorption of the iodide ion formed successively with an increase in the negative potentials. The adsorption phenomena of the corresponding bromides and chlorides are also discussed.

In a previous paper,[1] the electrode reaction mechanism of the bromide ion, the tribromomercurate ion, and mercuric bromide in dimethylformamide (DMF) was studied with the dropping mercury electrode. The results of d.c. polarography and large-scale electrolysis at a controlled potential indicated that two well-defined anodic waves given by the bromide ion can be attributed to the formation of the tribromomercurate ion and mercuric bromide by this reaction sequence:

$$2Hg + 6Br^- \rightleftharpoons 2HgBr_3^- + 4e \qquad (1)$$

$$Hg + 2HgBr_3^- \rightleftharpoons 3HgBr_2 + 2e \qquad (2)$$

The present study was undertaken in order to extend the previous study of the bromides to the corresponding iodides, namely, the iodide ion, the triiodomercurate ion, and mercuric iodide. Also, the adsorption phenomena of these depolarizers on the electrode surface were studied by the measurements of the oscillographic polarograms with a multi-triangular voltage sweep and of the electrocapillary curves. The adsorption phenomena of halide ions on the surface of the dropping mercury electrode have been extensively studied in aqueous

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solution,[2-6] but scarecely studied at all in non-aqueous solutions. The adsorption of the bromide ion on the electrode surface has been suggested[1] on the basis of the partial deviation from linearity of the log plot of the more negative wave, but the phenomenon has not been studied in detail.

Experimental

Materials. The DMF was purified as has been described previously,[1] except that distillation was carried out in the presence of a few lumps of calcium hydride. The tetraethylammonium perchlorate, used as a supporting electrolyte, was prepared as has been described by Fujinaga *et al.*[7] The tetraethylammonium iodide was prepared according to the directions of Given, Peover, and Schoen.[8] The tetraethylammonium bromide was prepared as has been described in a previous paper.[1] The tetraethylammonium chloride was prepared by neutralizing an aqueous solution of tetraethylammonium hydroxide with an equivalent quantity of hydrochloric acid. Mercuric iodide, bromide, and chloride obtained commercially were purified by recrystallizing them from ethanol. The polyvinyl chloride (PVC), used as a maximum suppressor, was obtained commercially. The degree of polymerization was about 1000.

Apparatus. D.c. polarography, large-scale electrolysis at a controlled potential, and conductivity measurements were carried out as have been described previously.[1] Likewise, all the potential measurements were referred to the aqueous saturated calomel electrode connected with the test solution by a DMF-agar salt bridge.[9] The dropping mercury electrodes used had the following characteristics in a 0.10M solution of tetraethylammonium perchlorate in DMF (open circuit): (1) $m=1.165$ mg/sec, $t=5.60$ sec for $h=66.0$ cm, (2) $m=1.540$ mg/sec, $t=4.50$ sec for $h=66.0$ cm.

The oscillographic polarograms were obtained using an apparatus similar in construction to that of Shinagawa *et al.*[10] An isosceles triangular voltage sweep obtained by integrating a square-wave voltage was amplified and then applied to the electrode alternatively. The polarographic cell used was the same as that used for d.c. polarography. In order to minimize the *iR* drop yielded across the cell, a fairly concentrated electrolyte solution (0.50M of tetraethylammonium perchlorate) was used. No test solutions were degassed. The two-electrode system with the dropping mercury electrode and the mercury pool electrode was used. The mercury pool electrode in 0.50M of tetraethylammonium perchlorate did not always provide a stable reference potential, but the variation in the reference potential was so small that it did not prevent us from observing electrochemical phenomena. The current-potential curves were observed on a dual-beam cathode-ray oscilloscope VC-6 of the Nihon Kohden Kogyo Co., which had a relatively high sensitivity up to 1.0 mV/cm. The horizontal sweep of the cathode-ray oscilloscope was synchronized with the frequency of an applied potential. The vertical deflection was proportional to the current flowing through the polarographic cell, so that the resulting trace had an *i-E* relationship. The oscillographic pattern of the trace was recorded on Fuji Neopan SS film using a Canon Pellix camera. The sweep frequency used for the oscillographic polarography was kept constant at 20 Hz.

Results and Discussion

Complex Formation between Tetraethylammonium Iodide and Mercuric Iodide in DMF. In order to elucidate the anodic dissolution mechanism of mercury in the presence of the halide ion, it is necessary to know what kinds of mercury complexes are formed between the mercuric or mercurous cation and the halide ion in solution. For example, it has been reported that, in an aqueous solution, the bromide ion depolarizes the dropping mercury electrode with the formation of mercurous bromide,[11] which is the most stable species in water. In DMF, however, mercurous bromide is less stable than either the tribromomercurate ion or mercuric bromide, so in DMF the bromide ion gives two anodic waves which correspond to the formation of the latter.[1]

Mercuric iodide is extremely soluble in DMF (*ca.* 4M at 20°C[12]) and stable in the solution. On the other hand, mercurous iodide is essentially insoluble in DMF and decomposes in part to mercury and mercuric iodide. Accordingly, when a dilute solution of the iodide ion is polarographically studied in DMF, it is not necessary to consider the formation of mercurous iodide.

Mercuric iodide has been reported to form a complex ion with the iodide ion in DMF.[12,13] The resulting complex ion has been thought to be the tetraiodomercurate ion (HgI_4^{2-}), formed from one mole of mercuric iodide and two moles of the iodide ion. However, in the case of the corresponding bromides it has been shown,[1] by means of conductometric titration, that the complex ion formed

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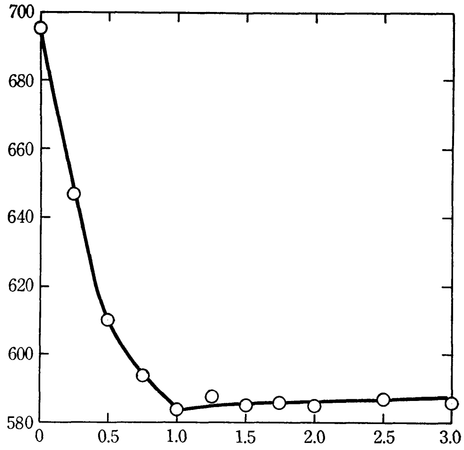

Fig. 1. Effect of HgI_2 on specific conductance of 10 mM Et_4NI in DMF at 25°C.

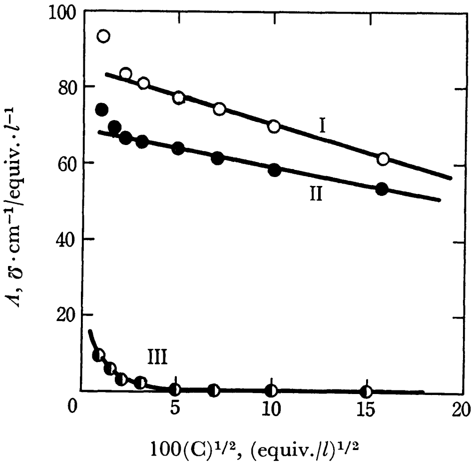

Fig. 2. Equivalent conductivities of Et_4NI (I), Et_4NHgI_3 (II), and HgI_2 (III) *vs.* square root of concentration in DMF at 25°C.

from mercuric bromide and the bromide ion was the tribromomercurate ion ($HgBr_3^-$) rather than the tetrabromomercurate ion ($HgBr_4^{2-}$). Consequently, the composition of the complex ion between mercuric iodide and the iodide ion was reexamined by the same method. The results are given in Fig. 1.

The addition of mercuric iodide to the solution of tetraethylammonium iodide in DMF lowered the specific conductivity, which reached the minimum value when the mole-ratio became equal to one. This obviously suggests that the complex formation occurs in solution and that the resulting complex ion is the triiodomercurate ion (HgI_3^-). The line in Fig. 1 curves also at the point where the mole-ratio is equal to 0.5. This suggests that the tetraiodomercurate ion may be formed in solution when the concentration of the iodide ion is more than double that of mercuric iodide.

The complex formation between mercuric iodide and the iodide ion can be confirmed by the data from the UV spectrum, too. The spectrum of the mixture of the iodide ion and the mercuric iodide equivalent in concentration has a strong absorption maximum at 304 mμ ($\varepsilon = 1.1 \times 10^5$), while neither mercuric iodide nor tetraethylammonium iodide shows such a maximum in the same wavelength region.

The equivalent conductivities of tetraethylammonium iodide, tetraethylammonium triiodomercurate, and mercuric iodide are plotted as a function of the square root of the concentration in Fig. 2. The data for tetraethylammonium iodide and tetraethylammonium triiodomercurate fit the Onsager equation, indicating that these salts behave as strong electrolytes in DMF. The equivalent conductivity of mercuric iodide is very low and does not fit the Onsager equation, showing that it is a weak electrolyte in DMF.

D. c. Polarography. A. Tetraethylammonium Iodide as Depolarizer. Using anhydrous DMF as a solvent, with 0.10M tetraethylammonium perchlorate as a supporting electrolyte, the d.c. polarographic behavior of tetraethylammonium iodide was investigated. This depolarizer gave two well-defined anodic waves (Fig. 3). The ratio between the heights of these waves was approximately 2 : 1, as was observed for tetraethylammonium bromide. The half-wave potentials ($E_{1/2}$) and the diffusion current constants (I_d) in various concentrations are given in Table 1. The I_d's of both the waves were practically constant over the concentration range studied. The limiting currents

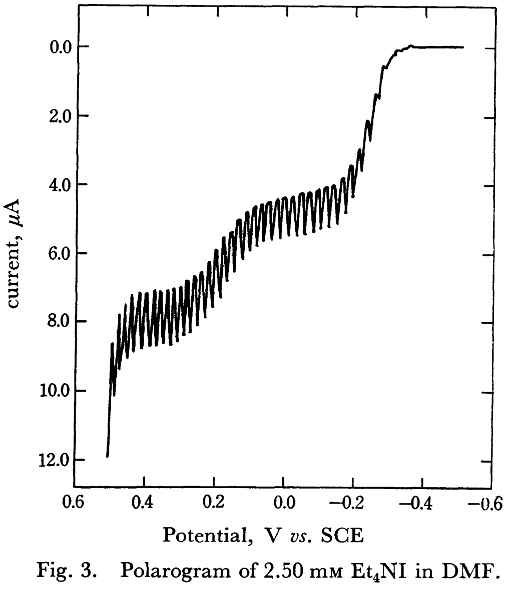

Fig. 3. Polarogram of 2.50 mM Et_4NI in DMF.

Table 1. Polarographic behavior of tetraethylammonium iodide in DMF at 25±0.1°C

Concn. (mM)	$E_{1/2}$ (V *vs.* SCE)		I_d	
	more pos.	more neg.	more pos.	more neg.
0.10	+0.130	−0.183	0.61	1.22
0.25	+0.135	−0.189	0.76	1.19
0.50	+0.153	−0.202	0.57	1.28
1.00	+0.155	−0.225	0.68	1.30
2.50	+0.168	−0.250	0.68	1.29
5.00	+0.175	−0.278	0.58	1.26

Table 2. Relation between the limiting current (i_d) of 0.50 mM of tetraethylammonium iodide and the effective pressure ($h_{corr.}$) on the dropping mercury electrode

$h_{corr.}$ (cm)	i_d (μA)		$i_d/(h_{corr.})^{1/2}$	
	more pos.	more neg.	more pos.	more neg.
84.3	0.450	1.14	0.049	0.124
74.3	0.430	1.06	0.050	0.123
64.3	0.425	1.01	0.053	0.126
54.3	0.395	0.90	0.053	0.122
44.3	0.345	0.83	0.052	0.123
38.3	0.325	0.77	0.052	0.124

for 0.50 mM of the depolarizer were found to be proportional to the square root of the effective pressure of mercury applied to the dropping mercury electrode (Table 2). These results indicate that the limiting currents of the two waves are diffusion-controlled.

The polarographic waves of the iodide ion are so similar to those of the bromide ion that the electrode-reaction mechanism proposed for the latter may also be presumed to hold for the former (Eqs. (3) and (4)):

$$2\mathrm{Hg} + 6\mathrm{I}^- \rightleftharpoons 2\mathrm{HgI_3}^- + 4e \qquad (3)$$

$$\mathrm{Hg} + 2\mathrm{HgI_3}^- \rightleftharpoons 3\mathrm{HgI_2} + 2e \qquad (4)$$

This mechanism was substantiated by analyzing the polarographic waves as follows. If the electrode reactions (3) and (4) are reversible, the equations of the waves are expressed by:

$$E_n = C_n + (\boldsymbol{RT}/2\boldsymbol{F}) \ln i/(i_d-i)^3 \qquad (5)$$

$$E_p = C_p + (\boldsymbol{RT}/2\boldsymbol{F}) \ln i^3/(i_d-i)^2 \qquad (6)$$

where E_n and E_p denote the potential of the electrode for the more negative and the more positive waves respectively, and where C_n and C_p are constant. These equations show that the half-wave potentials should change with i_d or with the concentration of the iodide ion according to:

$$E_{n,1/2} = C'_n - (\boldsymbol{RT}/\boldsymbol{F}) \ln i_d \qquad (7)$$

$$E_{p,1/2} = C'_p + (\boldsymbol{RT}/2\boldsymbol{F}) \ln i_d \qquad (8)$$

The results of the analysis of the waves are given in Fig. 4. The log plot for the more positive wave was a fairly good straight line, with a slope equal to 0.032 V, which is in fair agreement with the theoretical value of 0.030 V. The log plot for the more negative wave was also linear, with a slope equal to 0.030 V, over the greater part of the potential range. However, it became somewhat curved in the more negative region of potential, just as was observed in the case of the bromide ion.[1] As was suggested in the previous paper, this is probably due to the adsorption of the iodide ion on the surface of the dropping mercury electrode before depolarizing. The deviation can also be considered to be due in part to the formation of the tetraiodomercurate ion in the more negative part of the wave, where the concentration of the iodide ion on the mercury drop is much higher than that of mercuric

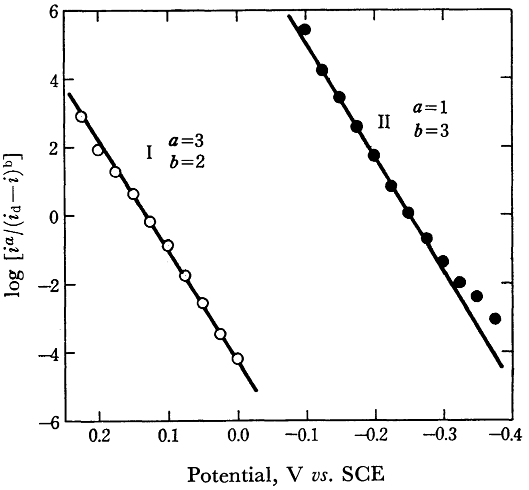

Fig. 4. Analysis of the waves of 0.50 mM $\mathrm{Et_4NI}$.
Slope: (I) 0.032; (II) 0.030

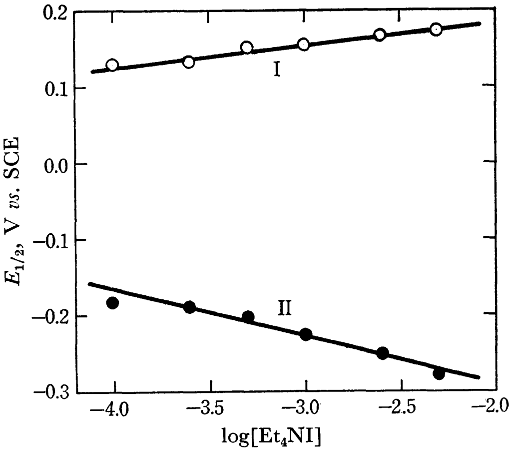

Fig. 5. Effect of concentration of $\mathrm{Et_4NI}$ on its half-wave potential.
Slope: (I), 0.030; (II), −0.060

ion dissolved.

The relation between the half-wave potential and the concentration of the depolarizer is plotted in Fig. 5. Straight-line relations were obtained for the waves with slopes equal to −0.060 V for the more negative wave (calculated for Eq. (7): −0.059 V) and 0.030 V for the more positive wave (calculated for Eq. (8): 0.030 V). All these results indicate that Eqs. (3) and (4) are both valid.

B. Mercuric Iodide. If Eqs. (3) and (4) are both valid, mercuric iodide should give two cathodic waves according to the following reactions:

$$3HgI_2 + 2e \rightleftharpoons Hg + 2HgI_3^- \quad (9)$$

$$2HgI_3^- + 4e \rightleftharpoons 2Hg + 6I^- \quad (10)$$

Actually, mercuric iodide gave two cathodic waves, though a maximum appeared on the more negative one (Fig. 6-I). In order to suppress the maximum, a small amount of PVC was dissolved in the test solution. PVC was reported to suppress all the maximum waves of thallium(I), lead(II), cadmium(II), and zinc(II) in *N*,*N*-dimethylacetamide.[14] As is shown in Fig. 6-II, PVC was found to suppress the maximum of mercuric iodide very effectively. In the concentration range from 0.003 to 0.007%, PVC acted as a satisfactory suppressor and had no effect on either the half-wave potential or the diffusion-current constant. At concentrations lower than 0.002% as well as higher than 0.010%, the effect of PVC became weak.

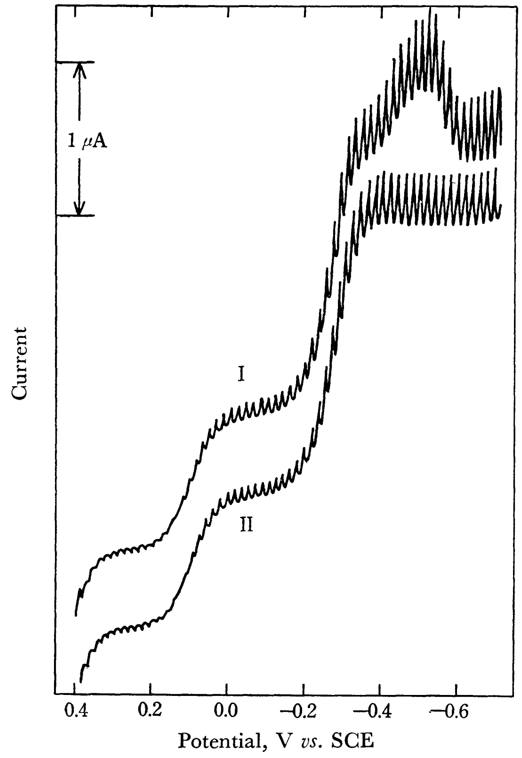

Fig. 6. Polarograms of 0.50 mM HgI_2 in DMF; (I) without PVC and (II) with 0.005% PVC.

TABLE 3. POLAROGRAPHIC BEHAVIOR OF MERCURIC IODIDE IN DMF CONTAINING 0.005% OF PVC AT 25±0.1°C

Concn. (mM)	$E_{1/2}$ (V *vs.* SCE)		I_d	
	more pos.	more neg.	more pos.	more neg.
0.10	+0.121	−0.210	1.05	2.29
0.25	+0.124	−0.231	0.73	2.40
0.50	+0.128	−0.242	1.08	2.36
1.00	+0.142	−0.260	1.10	2.34
2.50	+0.144	−0.279	1.14	2.39

TABLE 4. RELATION BETWEEN i_d OF 0.50 MM OF MERCURIC IODIDE AND $h_{corr.}$

$h_{corr.}$ (cm)	i_d (μA)		$i_d/(h_{corr.})^{1/2}$	
	more pos.	more neg.	more pos.	more neg.
84.3	0.90	2.10	0.098	0.228
74.3	0.84	1.98	0.098	0.230
64.3	0.75	1.80	0.094	0.226
54.3	0.73	1.70	0.099	0.230
44.3	0.65	1.50	0.097	0.224
38.3	0.58	1.40	0.094	0.226

The polarographic characteristics of mercuric iodide at various concentrations in the presence of 0.005% of PVC are given in Table 3. The limiting currents of both the waves were proportional to the concentration and to the square root of the effective pressure of mercury applied to the dropping mercury electrode (Table 4), indicating that they are diffusion-controlled.

The waves of mercuric iodide were analyzed in the same way as those of tetraethylammonium iodide. The results showed that the waves are in fair agreement with those given theoretically by Eqs. (11) and (12).

$$E'_p = C''_p - (RT/2F) \ln i^2/(i_d - i)^3 \quad (11)$$

$$E'_n = C''_n - (RT/2F) \ln i^3/(i_d - i) \quad (12)$$

The shift of the half-wave potential with i_d is given by Eqs. (7) and (8), which were accepted to hold as is shown by the results in Table 3.

C. Tetraethylammonium Triiodomercurate. As was to be expected from Eqs. (4) and (10), tetraethylammonium triiodomercurate gives two waves, anodic and cathodic, and on the latter a maximum arises (Fig. 7-I). The maximum was also suppressed by the addition of 0.005% of PVC (Fig. 7-II). The polarographic behavior is summarized in Table 5. Analysis of the current-voltage curves showed that the anodic wave is ex-

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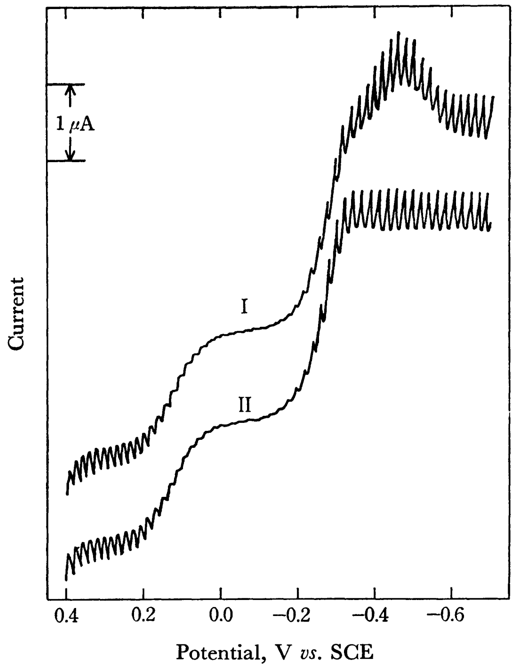

Fig. 7. Polarograms of 0.50 mM Et_4NHgI_3 in DMF, (I) without PVC and (II) with 0.005% PVC.

TABLE 5. POLAROGRAPHIC BEHAVIOR OF TETRAETHYLAMMONIUM TRIIODOMERCURATE IN DMF CONTAINING 0.005% OF PVC at 25±0.1°C

Concn. (mM)	$E_{1/2}$ (V vs. SCE)		I_d	
	more pos.	more neg.	more pos.	more neg.
0.10	+0.107	−0.226	0.91	3.32
0.25	+0.126	−0.246	1.87	3.56
0.50	+0.129	−0.264	1.70	3.46
1.00	+0.149	−0.269	1.72	3.42
2.50	+0.169	−0.282	1.63	3.06

pressed by Eq. (6), and the cathodic wave, by Eq. (12).

Controlled Potential Electrolysis of Mercuric Iodide. Further evidence for the electrode-reaction mechanism postulated above was obtained by a large-scale electrolysis of mercuric iodide at a mercury pool cathode with a controlled potential. Electrolytic reduction at a potential of the plateau of the more positive wave yielded tetraethylammonium triiodomercurate, the formation of which was confirmed by measuring the polarogram and the UV spectrum of the catholyte. The quantity of electricity transferred per mole of the depolarizer (n=0.64 F) virtually agreed with that calculated for Eq. (9) (n=0.67 F). As was expected from Eq. (10), tetraethylammonium iodide, identified by the polarogram of the catholyte, was obtained by the electroreduction of mercuric iodide at a potential of the plateau of the more negative wave. The value of n (n=2.21 F) also agreed with that calculated for Eqs. (9) and (10) (n=2.00 F).

Oscillographic Polarography of Tetraethylammonium Iodide. In order to investigate the polarographic behavior of tetraethylammonium iodide in more detail, an isosceles-triangular voltage sweep was applied to polarize the dropping mercury electrode alternatively. A current-potential curve obtained on a cathode-ray oscilloscope is shown in Fig. 8-I. It may be inferred at sight that the anodic peaks, A and B, are due to the step-by-step oxidation of mercury to the triiodomercurate ion and to mercuric iodide respectively. The cathodic peaks, C and D, probably correspond to the step-by-step re-reduction of mercuric iodide to the triiodomercurate ion and to the iodide ion respectively.

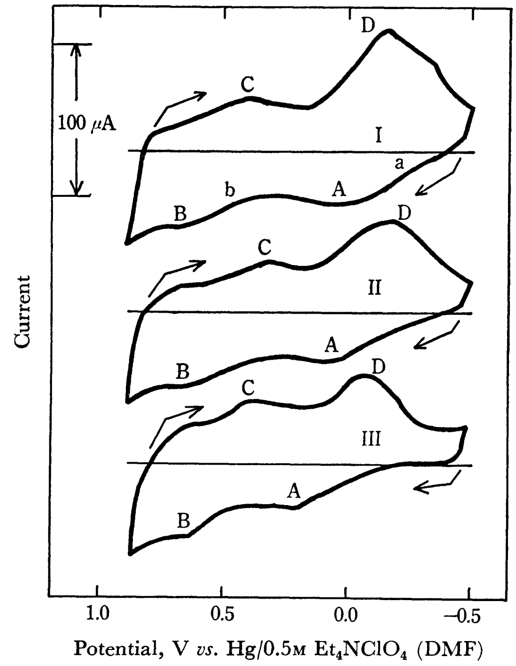

Fig. 8. Oscillographic polarograms of Et_4NI (I), Et_4NBr (II), and Et_4NCl (III) in DMF.

It is noticeable that the base line of the anodic peaks goes down as the positive potential increases, whereas that of the cathodic peaks remains essentially the same. Furthermore, it is remarkable that the peak D is exceptionally higher than the other peaks, A, B, and C. The peak D is so high that it cannot be considered that the whole current is due only to the re-reduction of the triiodomercurate ion formed in the preceeding electrooxidation and re-reduction processes. These results indicate that not only the electron transfer process, but also the adsorption-desorption process, occurs on the electrode surface.

The species which can be adsorbed on the electrode are the iodide ion, the triiodomercurate ion, and mercuric iodide. In the anodic scan, the adsorption of these depolarizers may cause the increase in the anodic charging current. Since the iodide ion is the only depolarizer existing in the solution before electrolysis, the moderate increase in the charging current shown by the curve a may be due to the successive adsorption of the iodide ion on the electrode surface. At the potential close to the peak A, the iodide ion adsorbed is converted into the triiodomercurate ion as a result of its reaction with the mercuric ion formed by the electrooxidation of mercury. The resulting triiodomercurate ion may also be adsorbed on the electrode surface, so the double-layer capacity may gradually increase with an increase in the amount of the adsorbate during electrolysis (curve b). At the potential near the peak B, the triiodomercurate ion adsorbed is further converted into mercuric iodide, which may also be adsorbed on the electrode surface, and a considerable charging current flows consecutively.

In the cathodic scan, on the other hand, the desorption of the depolarizers can cause an increase in the cathodic charging current. However, when mercuric iodide is re-reduced to mercury and the triiodomercurate ion at the potential close to the peak C, both mercuric iodide and the triiodomercurate ion may be strongly adsorbed on the electrode surface. Consequently, the double-layer capacity may scarecely change, and the base line of the cathodic scan remains essentially the same. At the potential near the peak D, the triiodomercurate ion is reduced to mercury and the iodide ion. The resulting iodide ion may be abruptly desorbed from the electrode surface with an increase in the negative potential. As a result, a large quantity of charging current flows (the peak D).

Considering that the potential of the maximum, which arises on the reduction wave of the triiodomercurate ion, is close to that at which the iodide ion is abruptly desorbed, we might be able to relate the desorption phenomena to the appearance of the polarographic maximum as follows. It has been confirmed that the current density at the bottom of the mercury drop is greater than that at the top as a result of the screaning effect of the tip of the capillary.[15] If the iodide ion, which is formed by the reduction of the triiodomercurate ion adsorbed on the electrode surface, is abruptly desorbed from the electrode surface, the difference in current density must cause an unequal distribution of the triiodomercurate ion in the double layer at the bottom and at the top of the mercury drop, which may also cause a tangental potential gradient in the double layer around the mercury drop, as well as the difference in surface tension between that at the bottom and that at the top of the drop. Consequently, the interface is pulled from top to bottom. The resulting streaming of the double layer and mercury in the drop may be responsible for the polarographic maximum. The maximum may not disappear until the potential of the mercury electrode becomes too negative for the triiodomercurate ion to adsorb on the electrode surface. The PVC added to the solution as a maximum suppressor may be adsorbed on the electrode surface with the formation of a thin film, which may prevent the iodide ion from being abruptly desorbed from the electrode surface. In the case of the electrooxidation of mercury in the presence of the iodide ion, the iodide ion may be supplied to the electrode surface by diffusion, and so no convection of the electrode can occur. Although the above description of the cause of the polarographic maximum is plausible, it is no more than a speculation; further experimental data are necessary before we can discuss it conclusively.

The oscillographic polarograms of tetraethylammonium bromide and chloride (Fig. 8-II and -III) were very similar to those of the corresponding iodide, but with some differences. The most remarkable difference was that the heights of the peaks D of I^-, Br^-, and Cl^- decrease in that order. This clearly indicates that the peak D is due not only to the electron-transfer process, but also to the nonfaradic desorption process. Furthermore, it was ascertained that the adsorptive activities of the triiodomercurate ion, the tribromomercurate ion, and the trichloromercurate ion decrease in that order.

Electrocapillary Curve. The adsorption phenomena of the halides were also studied by the measurement of the electrocapillary curves. The

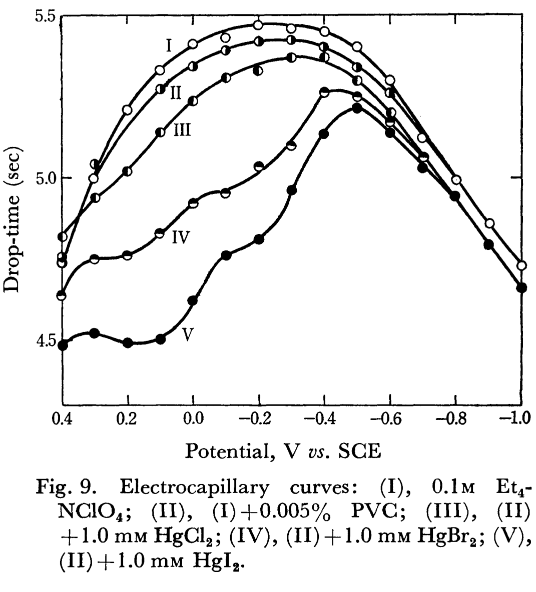

Fig. 9. Electrocapillary curves: (I), 0.1M Et_4NClO_4; (II), (I)+0.005% PVC; (III), (II)+1.0 mM $HgCl_2$; (IV), (II)+1.0 mM $HgBr_2$; (V), (II)+1.0 mM HgI_2.

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[15] I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed., Vol. I, Interscience Publishers, New York (1952), p. 176.

effect of 1.0 mM of mercuric halide on the shape of the electrocapillary curve is shown in Fig. 9. The electrocapillary curve in the presence of 2.0 mM of tetraethylammonium iodide was essentially identical with that in the presence of 1.0 mM of mercuric iodide.

In the presence of mercuric iodide, a marked decrease in the surface tension was observed in the potential region between +0.4 and −0.8 V *vs.* SCE. Considering the electrode reaction mechanism elucidated above, it can be presumed that the decrease in the drop time in the potential region between +0.4 and +0.2 V *vs.* SCE is due to the adsorption of mercuric iodide. Similarly, the decrease in the surface tension in the potential range between +0.1 and −0.1 V *vs.* SCE and that between −0.3 and −0.8 V *vs.* SCE may correspond to the adsorption of the triiodomercurate ion and the iodide ion respectively on the electrode surface.

The results in Fig. 9 also reveal that the iodide ion and its mercuric complexes are the most capillary-active. The bromide ion and its mercuric complexes are less strongly adsorbed on the electrode surface. The chloride ion and its mercuric complexes are only slightly capillary-active.

The effect of PVC on the shape of the electrocapillary curve is also shown in Fig. 9. The addition of a small amount of PVC caused a slight decrease in the drop time of the mercury in the potential region more positive than −0.7 V *vs.* SCE. It is apparent that the adsorption of PVC on the electrode surface occurs, this may prevent the convection of the mercury drop and, consequently, the appearance of the maximum. All the results mentioned here are in fair agreement with those obtained by oscillographic polarography.