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Polarography of Halides in Dimethylformamide. I. Bromide Ion and Its Mercuric Compounds

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The complex formation between tetraethylammonium bromide (TEB) and mercuric bromide in dimethylformamide was observed conductometrically, and a complex, tetraethylammonium tribromomercurate (TETM), was isolated. Voltammetric studies of TEB, TETM, and mercuric bromide were made, using the dropping mercury electrode in dimethylformamide containing 0.1 M tetraethylammonium perchlorate. It was found that TEB gives two reversible anodic waves, of which the more negative one is due to the oxidation of mercury to TETM, and the more positive, to the oxidation of mercury to mercuric bromide. The electrode reaction mechanism was also investigated by means of large-scale electrolysis with a controlled potential.

At the dropping mercury electrode the halide ion gives a reversible anodic wave due to the oxidation of mercury to halogenated mercury species. For example, it is well known that the halide ion in water depolarizes the dropping mercury electrode upon the formation of insoluble mercurous halide.[1]

However, the polarographic behavior of halide ions in dimethylformamide (DMF) has been shown to differ from that in water.[2,3] Given and Peover[2] observed that the iodide ion in DMF gives two anodic waves, of which the more negative may be attributed to the oxidation of mercury to the tetraiodomercurate ion on the basis of the analysis of the wave. The more positive wave was suggested to arise from the oxidation of mercury to the triiodomercurate ion, but it was not proved experimentally. They also reported that the chloride ion in DMF showed virtually the same polarographic behavior as the iodide ion except for some departures of the more negative wave from that to be expected on the basis of the equation of the wave, probably as a result of the partial dissociation of the tetrachloromercurate ion to the trichloromercurate ion and the chloride ion. The behavior of the bromide ion in DMF was studied by Breant and Kiet,[3] who reported the formation of the tetrabromomercurate ion by the oxidation of mercury. However, the behavior of these halide ions on the electrode surface has still remained obscure, especially the electrode reaction mechanism at the potential of the more positive wave.

In the present paper, the polarographic behavior of the bromide ion and its mercuric compounds in DMF will be examined in detail in order to make clearer the mechanism of the electrooxidation of mercury; we will use the methods of d. c. polarography, large-scale electrolysis with a controlled potential, and conductometry.

Experimental

Materials. DMF obtained commercially was purified by the method of Wawzonek *et al.*[4] (bp 51.0—52.3°C/18 mmHg). Tetraethylammonium perchlorate

1) I. M. Kolthoff and C. S. Miller, *J. Am. Chem. Soc.*, **63**, 1405 (1941).
2) P. H. Given and M. E. Peover, *J. Chem. Soc.*, **1959**, 1602.
3) M. Breant and N. V. Kiet, *Compt. Rend.*, **262**, 955 (1966).
4) S. Wawzonek, E. W. Blaha, R. Berkey and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955).

(TEP) was prepared from tetraethylammonium hydroxide and perchloric acid according to the directions of Geske and Maki.[5] The crude product was recrystallized twice from water and dried in a vacuum oven at 65°C. The 0.10 M solution of TEP in DMF showed virtually no polarographic wave within the range from +0.4 to −2.7 V *vs.* SCE. Tetraethylammonium bromide (TEB) was prepared according to the directions of Fleischer and Nachod.[6]

Found: Br, 37.77%. Calcd for $C_8H_{20}NBr$: Br, 38.02%.

Mercuric bromide obtained commercially was purified by recrystallizing it from ethanol-water. A reagent-grade sample of mercurous bromide was used without further purification.

Tetraethylammonium Tribromomercurate (TETM). This was prepared by a method similar to that described by Cruse, Goertz, and Petermöller.[7] Mercuric bromide (3.60 g) and TEB (2.10 g) were added to 30 m*l* of DMF and stirred until they were in solution. The solution was then poured into 150 m*l* of water; the precipitate was collected by filtration, washed with water, and recrystallized from DMF-ethanol. There was thus obtained 2.2 g (39%) of TETM, which had the following characteristics: mp 138.0—139.5°C (lit.[7] mp 124°C), IR (KBr disk): 1456 and 1402 cm^{-1} (δ C–H), 1183 and 1030 cm^{-1} (ν C–N).

Found: C, 16.83; N, 2.63%. Calcd for $C_8H_{20}NHgBr_3$: C, 16.84; N, 2.46%.

Conductivity Measurements. A Yanagimoto conductivity outfit (model MY-7) was used for these measurements. A conductivity cell was fitted with circular, blacked platinum electrodes separated by 10 mm. The cell constant was 0.4455. All the measurements were made at 25±0.1°C.

Polarographic Measurements. Anhydrous DMF was used as a solvent, with 0.10 M TEP as the supporting electrolyte. An H-type cell was used for the polarography. The current-potential curves were recorded with a Shimadzu polarograph, model RP-50. The bridged saturated calomel electrode proposed by Takaoka[8] was used throughout as a reference electrode. All the potentials were corrected for the bridge potentials measured in the way described in the literature. The potential drifting during one polarographic measurement was less than ±5 mV. All the potentials were corrected automatically for the IR-drop across the electrolysis cell with a Shimadzu automatic potential corrector, model AIC-50. The dropping mercury electrode had the following characteristics in a 0.10 M solution of TEP in DMF (open circuit): m=1.165 mg/sec and t= 5.6 sec for h=66.0 cm. All the measurements were made at 25±0.1°C.

Large-Scale Electrolysis with Controlled Potential. Electrolysis was carried out in a cell similar in construction to that used by Fujinaga *et al.*[9] The mercury pool and the platinum electrode used had areas of approximately 75 and 60 cm^2 respectively. The bridged saturated calomel electrode mentioned above was used as a reference electrode. The potential of the mercury pool was controlled with an improved Yanagimoto VE-3 controlled potential electrolyser.

A solution of 300 m*l* of DMF with 6.89 g of TEP, and 3.60 g of mercuric bromide or 1.26 g of TEB was degassed for 2 hr with pure nitrogen, and then electrolyzed at a controlled potential with stirring and with cooling in an ice bath (3—5°C). The quantity of electricity required for the electrolysis was estimated graphically from the current-time curve. After the electrolysis, the electrolyte was concentrated by vacuum distillation to about 20 m*l*. The products were isolated by fractional crystallization from water. All the products were identified by their melting points, IR spectra, elementary analyses, and/or polarograms.

Results and Discussion

Solubility Relations. TEB and mercuric bromide are easily soluble in DMF, while mercurous bromide is insoluble. If a concentrated solution of mercuric bromide in DMF is shaken with mercury, mercurous bromide precipitates at once, but if the solution is dilute enough (below 0.025 M at 25°C), no precipitation occurs. If a trace amount of mercurous bromide is shaken with DMF, it dissolves with the separation of mercury. These observations indicate that the equilibrium between mercuric and mercurous bromide (Eq. (1)) is established rapidly, and that the solubility of mercuric bromide in the presence of mercury is about 0.025 M at 25°C.

$$HgBr_2 + Hg \rightleftarrows Hg_2Br_2 \qquad (1)$$

Accordingly, when a dilute solution of mercuric bromide (below 0.005 M) is polarographically studied in DMF, it is not necessary to consider the reaction between mercuric bromide and mercury.

There is no separation of mercurous bromide when a concentrated solution of mercuric bromide in DMF is shaken with mercury in the presence of TEB. This suggests that the complex formation between mercuric bromide and TEB occurs in solution, as has been reported by Cruse et al. in the case of acetonitrile.[7]

Conductometric Measurements. If the complex formation between mercuric bromide and TEB occurs in DMF and if the value of the conductivity of the complex is different from those of the constituents, the mole-ratio between the constituents can be determined by the method of conductometric titration. The results of conductometric titration are given in Fig. 1. The addition of mercuric bromide to the solution of TEB in DMF lowered the specific conductivity, which reached the minimum value when the concentration of mercuric bromide added became equal to that of TEB. This obviously suggests that complex formation occurs in solution and that

5) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).
6) K. D. Fleischer and F. C. Nachod, *Anal. Chem.*, **33**, 208 (1961).
7) K. Cruse, E. P. Goertz and H. Petermöller, *Z. Elektrochem.*, **55**, 405 (1951).
8) K. Takaoka, *Rev. of Polarography*, **14**, 63 (1966).
9) T. Fujinaga, K. Takaoka, T. Nomura and K. Yoshikawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **89**, 185 (1968).

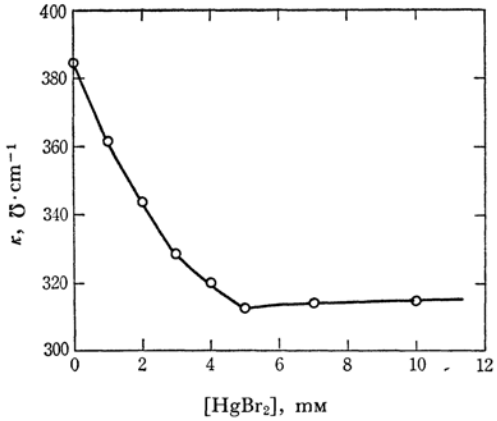

Fig. 1. Effect of $HgBr_2$ on specific conductance of 5 mM TEB in DMF at 25°C.

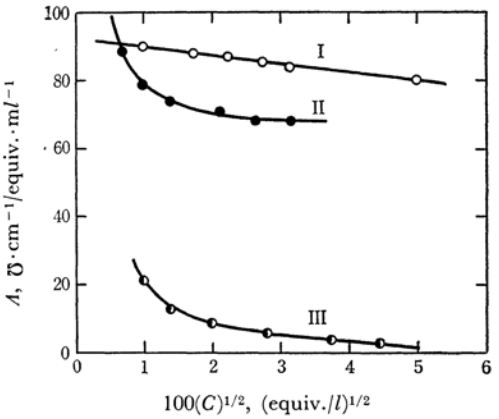

Fig. 2. Equivalent conductivities of TEB (I), TETM (II), and $HgBr_2$ (III) *vs.* square root of concentration in DMF at 25°C.

the mole-ratio between the constituents is equal to one. The equivalent conductivity of the mixture of mercuric bromide and TEB with the mole ratio of 1 : 1 is plotted in Fig. 2, together with those of the constituents.

The complex, TETM, was isolated as has been described in the Experimental section. The polarographic and conductometric behavior of this complex in DMF coincided with those of the mixture of the constituents with the mole ratio of 1 : 1. Irrespective of the presence or absence of mercury, TETM is easily soluble in DMF (about 50% by weight), while it is insoluble in water.

Polarographic Measurements. Using anhydrous DMF as a solvent with 0.10 M TEP as a supporting electrolyte, the polarographic behavior of TEB, TETM, and mercuric bromide was investigated (Fig. 3). TEB gives two anodic waves and no maximum over the potential range of +0.4——2.7 V *vs.* SCE in the concentrations studied. TETM gives two waves, anodic and cathodic; on the latter a maximum appears at concentrations above 0.25 mM. Mercuric bromide gives two cathodic waves, on the more negative wave of which a maximum arises in the concentrations above 0.50 mM. Since both of these maxima arise at a more negative potential of the more negative waves, they do not prevent us from estimating the half-wave potentials and the limiting currents of the more negative waves.

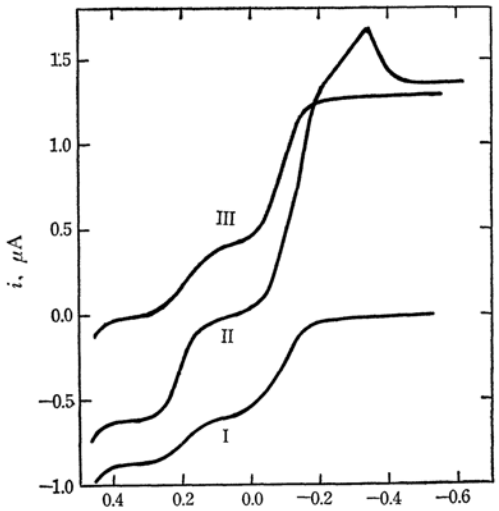

Fig. 3. Polarograms of the 0.25 mM solutions of TEB (I), TETM (II), and $HgBr_2$ (III) in DMF containing 0.10 M TEP at 25°C.

Table 1. Polarographic behavior of TEB, TETM, and mercuric bromide in DMF containing 0.10 M TEP at 25±0.1°C

Depolarizers	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.
TEB	0.10	+0.199	−0.092	0.80	2.02
	0.25	+0.205	−0.103	0.70	1.58
	0.50	+0.221	−0.114	0.74	1.52
	1.00	+0.234	−0.136	0.74	1.49
	2.50	+0.247	−0.159	0.69	1.55
	5.00	+0.264	−0.184	0.67	1.49
TETM	0.10	+0.191	−0.122	1.56	3.45
	0.25	+0.210	−0.137	1.61	3.66
	0.50	+0.219	−0.154	1.73	3.66
	1.00	+0.231	−0.170	1.95	3.54
	2.50	+0.247	−0.196	1.91	3.38
$HgBr_2$	0.10	+0.142	−0.073	1.10	2.33
	0.25	+0.171	−0.094	1.14	2.33
	0.50	+0.217	−0.121	1.27	2.36
	1.00	+0.225	−0.146	1.31	2.35
	2.50	+0.229	*	1.29	*
	5.00	+0.245	*	1.28	*

* Impossible to measure owing to the maxima.

Table 2. Relation between i_d of 0.50 mM TEB 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	0.60	1.24	0.065	0.135
74.3	0.55	1.12	0.064	0.130
64.3	0.52	1.05	0.065	0.131
54.4	0.47	0.97	0.064	0.131
44.4	0.42	0.85	0.064	0.129
38.4	0.40	0.78	0.065	0.126

The half-wave potentials ($E_{1/2}$) and the diffusion current constants (I_d) in various concentrations of these depolarizers are given in Table 1. All the I_d's were effectively constant over the concentration range studied. The limiting currents for 0.50 mM TEB were found to be proportional to the square root of the effective pressure of the mercury applied to the dropping mercury electrode (Table 2). Similar results were obtained for both TETM and mercuric bromide, indicating that the limiting currents of all these waves are diffusion-controlled.

The ratios of the I_d's of the more positive waves to those of the more negative waves caused by these depolarizers were approximately 1 : 2, suggesting that the ratios of the numbers of electrons transferred at the more positive wave to those transferred at the more negative wave may be 1 : 2. Assuming that the overall electroreduction of three molecules of mercuric bromide is due to the reversible transfer of six electrons from the dropping mercury electrode, yielding mercury and bromide ions, it follows that two electrons should be assigned to the more positive reduction process and four electrons to the more negative reduction process. A similar deduction may be made with regard to the electrooxidation of mercury in the presence of bromide ions. Thus, the mechanism of the electrode reactions may be given by:

$$3HgBr_2 + 2e \rightleftarrows Hg + 2HgBr_3^- \quad (2)$$

$$2HgBr_3^- + 4e \rightleftarrows 2Hg + 6Br^- \quad (3)$$

This mechanism can make clear the polarographic characteristics of TETM. Namely, it indicates that the more positive wave should be anodic, the more negative wave, cathodic, and the ratio between the I_d's, 1 : 2.

This hypothetical mechanism was substantiated by analyzing the waves of complex mercury ions studied by Kolthoff and Miller.[1] By applying their method to this mechanism, the potential of the dropping mercury electrode is given for the more positive wave by:

$$E_p = C_p + (\boldsymbol{RT}/2\boldsymbol{F}) \ln ([HgBr_2]_0^3/[HgBr_3^-]_0^2) \quad (4)$$

and for the more negative wave by:

$$E_n = C_n + (\boldsymbol{RT}/2\boldsymbol{F}) \ln ([HgBr_3^-]_0/[Br^-]_0^3) \quad (5)$$

where the subscript zero denotes the concentration at the surface of the dropping mercury electrode, and where C_p and C_n are constant. It can easily be shown that the equations of the waves of bromide ion are:

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

$$E_n = C_n' + (\boldsymbol{RT}/2\boldsymbol{F}) \ln [i/(i_d - i)^3] \quad (7)$$

These equations show that the half-wave potentials should change with i_d or with the concentrations of bromide ion according to:

$$E_{p,1/2} = C_p'' + (\boldsymbol{RT}/2\boldsymbol{F}) \ln [Br^-] \quad (8)$$

$$E_{n,1/2} = C_n'' - (\boldsymbol{RT}/\boldsymbol{F}) \ln [Br^-] \quad (9)$$

The results of the analyses of the waves are given in Fig. 4. The plotting of $\log[i^3/(i_d-i)^2]$ against the potential for the more positive wave gave a fairly good straight line, with a slope equal to 0.032 V (calculated for Eq. (6); 0.030 V), indicating that Eq. (2) is valid. The plot of $\log [i/(i_d-i)^3]$ against the potential for the more

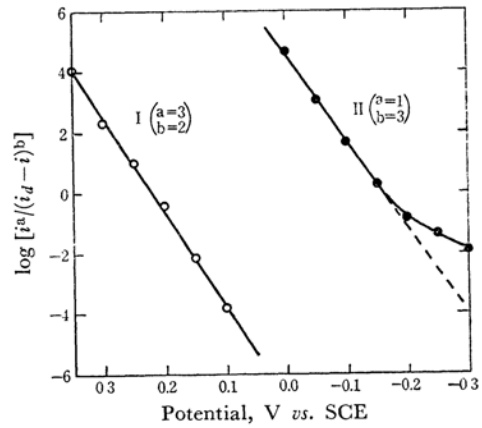

Fig. 4. Analyses of the waves of 0.50 mM TEB.
Slope: (I), 0.032; (II), 0.034

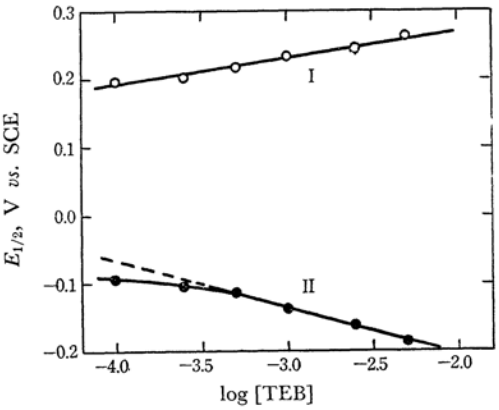

Fig. 5. Effect of concentration of TEB on its half-wave potential.
Slope: (I), 0.035; (II), −0.062

Table 3. Large-scale electrolysis of mercuric bromide and TEB with controlled potential in DMF containing 0.10 M TEP at 4±1°C

Depolarizers	E[a] (V *vs.* SCE)	Time (min)	i (μA) Start	i (μA) Finish	n[b] (F) Obsd	n[b] (F) Calcd[c]	Products (%)
$HgBr_2$[d]	+0.11	165	90	1.0	0.66	0.67	TETM (26)
$HgBr_2$[d]	−0.55	120	430	2.0	2.12	2.00	TEB (41)
TEB[e]	−0.04	395	185	2.0	1.01	0.67	TETM (40)
TEB[e]	+0.36	240	315	80.0	2.45	1.00	$HgBr_2$ (27)

a) Set potential for electrolysis.
b) Quantity of electricity used per one mole of depolarizer.
c) Calculated for Eq. (2) and/or (3).
d) Electroreduction with Hg cathode and Pt anode.
e) Electrooxidation with Hg anode and Pt cathode.

negative wave was also linear, with a slope equal to 0.034 V, over the greater part of the potential range, but it became curved at the more negative potentials (above −0.2 V *vs.* SCE), indicating a behavior different, probably due to the adsorption of bromide ions on the surface of the dropping mercury electrode, as has been shown by Biegler in an aqueous solution.[10]

The relation between the half-wave potentials and the concentrations of the bromide ion is plotted in Fig. 5. A straight line relation was obtained for the more positive wave with a slope equal to 0.035 V (calculated for Eq. (8); 0.030 V) and one for the more negative wave with a slope equal to −0.062 V (calculated for Eq. (9); −0.059 V), though the plot for the latter became somewhat curved at low concentrations. Similar studies were carried out concerning TETM and mercuric bromide; all the results agreed well with the equations derived from the mechanism postulated above.

Large-Scale Electrolysis with a Controlled Potential. In order to make sure of the electrode reaction mechanism, a large-scale electrolysis of mercuric bromide and TEB was carried out with a controlled potential in DMF. The results are given in Table 3.

The electroreduction of mercuric bromide with the Hg cathode at the potential of the plateau of the more positive wave yielded TETM (26%); the quantity of electricity transferred per mole of the depolarizer (n) was 0.66 F (calculated for Eq. (2); 0.67 F), indicating that Eq. (2) is valid. TEB was obtained (41%) by the electroreduction of mercuric bromide at the potential of the plateau of the more negative wave, and the value of n was equal to 2.12 F (calculated for Eq. (2) and (3); 2.00 F), indicating that Eq. (3) is also valid. The polarograms of the catholytes after electrolysis, in both cases, agreed closely with those of the products.

The electrooxidation of TEB with the Hg anode at the potential of the plateau of the more negative wave yielded TETM (40%), as expected, whereas the value of n (1.01 F) was much greater than that expected on the basis of Eq. (3) (0.67 F). The polarogram of the anolyte showed that there was considerable increase in the anoidc wave as well as in the wave of TETM, caused probably by the formation of oxidizable species at the cathode, but the details have not been studied. The electrooxidation of TEB at the potential of the plateau of the more positive wave yielded mercuric bromide (27%), as expected, while the value of n (2.45 F) was also much greater than that expected on the basis of Eqs. (2) and (3) (1.00 F).

The Mechanism of the Anodic Dissolution of Mercury in the Presence of the Bromide Ion in DMF. On the basis of the observations presented above, it is reasonable to conclude that the two anodic waves given by the bromide ions in DMF are due to oxidation of mercury to tribromomercurate ions (Eq. (3)) and to mercuric bromide (Eq. (2)). On the other hand, it has already been reported by Given and Peover[2] that halide ions in DMF depolarize the dropping mercury electrode, mainly forming tetrahalogenomercurate ions (HgX_4^{2-}). However, they also observed that the ratios between the I_d's of the two waves of these depolarizers are approximately 1 : 2, indicating the formation of trihalogenomercurate ions. We have also observed, by means of conductometric titration, that complex formation occurs between mercuric iodide and tetraethylammonium iodide in the mole ratio of 1 : 1. Accordingly, it may be necessary to reinvestigate the polarographic behavior of halide ions other than the bromide ion.

The mechanism proposed in the present paper is similar to that at such inert electrodes as platinum[11,12] and graphite[13] in DMF or acetonitrile, where halide ions also give two anodic

10) T. Biegler, *J. Electroanal. Chem.*, **6**, 365 (1963).

11) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 1852 (1957).
12) M. Breant and C. Sinicki, *Compt. Rend.*, **260**, 5016 (1965).
13) D. Dryhurst and P. J. Elving, *J. Electroanal. Chem.*, **12**, 416 (1966).

waves, one of which corresponds to that of the oxidation of halide ions (X^-) to trihalide ions (X_3^-), and the other, to that of trihalide ions to halogen molecules (X_2). Considering that both trihalide ions and halogen molecules react rapidly with mercury, it might be possible to divide the anodic dissolution processes of mercury into the oxidation stpes of halide ions and the reaction steps between the oxidized species and mercury as follows:

$$\begin{array}{ccccc} 6X^- & \rightleftharpoons & 2X_3^- + 4e & \rightleftharpoons & 3X_2 + 6e \\ & & \downarrow{\scriptstyle 2Hg} & & \downarrow{\scriptstyle 3Hg} \\ & & 3HgX_3^- & & 3HgX_2 \end{array} \qquad (10)$$

With this mechanism, however, it is difficult to explain that the anodic waves are reversible, because the reactions between mecury and trihalide ions and between mercury and halogen molecules are both certainly irreversible. According to this mechanism, it is also difficult to explain the polarographic behavior of TETM and mercuric bromide, indicating that this mechanism is implausible.

The polarographic behavior of the bromide ion in DMF is obviously different from that in water. This difference can be related to the difference in the stability of the mercury species in these solvents. It is well known that mercuric halides in water react with mercury even in a very dilute solution, forming insoluble mercurous halides.[14] On the other hand, we have observed that mercuric bromide in DMF remains inert to mercury even in a comparatively concentrated solution, as has been described above. TETM is reported to possess great stability in acetonitrile, but less stability in water.[7] We have also observed that it is very stable in DMF. Thus, in an aqueous solution the bromide ion depolarizes the dropping mercury electrode, thus forming mercurous bromide, 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 the bromide ion gives two anodic waves in DMF which correspond to the formation of the latter.

14) I. M. Kolthoff and C. S. Miller, *J. Am. Chem. Soc.*, **63**, 2732 (1941).