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Polarography of Halides in Dimethylformamide. IV. The Stability Constants of the Halo Complexes of Mercury (II)

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The overall stability constants (β) of mercuric halide and the tri- and tetrahalogenomercurate ions in dimethylformamide containing 0.1 M tetraethylammonium perchlorate were evaluated by the polarographic method at 25°C. The values of log β obtained were: 24.16 for $HgCl_2$, 31.23 for $HgCl_3^-$, 34.57 for $HgCl_4^{2-}$, 24.17 for $HgBr_2$, 31.62 for $HgBr_3^-$, 34.73 for $HgBr_4^{2-}$, 25.93 for HgI_2, 33.34 for HgI_3^-, and 36.02 for HgI_4^{2-}.

A number of workers have evaluated the stability constants of the halo complexes of mercury(II) in an aqueous solution,[1] but only a few workers have done so in non-aqueous solutions. Ellendt and Cruse[2] have evaluated the stepwise stability constants of the tri- and tetrahalogenomercurate ions in acetonitrile by means of conductivity measurements. Given and Peover[3] and Breant and Kiet[4] have determined the overall stability constants of the tetrahalogenomercurate ion in dimethylformamide (DMF) by the polarographic method. These results show that the halo complexes of mercury(II) are generally more stable in non-aqueous solutions than in an aqueous solution.

In the previous papers of this series,[5-7] the mechanism of the electrooxidation of mercury in the presence of the halide ion was studied in DMF by means of polarography; the current-potential curve thus obtained was interpreted on the basis of the formation of complex ions of the $HgX_j^{(2-j)}$ type, where j has values from 2 to 4. In the present experiment, the overall stability constants of these complex ions were determined in DMF containing 0.1 M tetraethylammonium perchlorate by means of an analysis of the d.c. polarographic waves.

Experimental

The solvent and the supporting electrolyte used were purified as has been described previously.[6] Polarograms were obtained in a manner similar to that described before. Likewise, all the potentials reported in the present paper refer to an aqueous, saturated calomel electrode connected with a test solution by a DMF-agar salt bridge.[8]

Preparation of Solutions of Mercuric Perchlorate in DMF. According to the directions of Given and Peover,[3] mercuric perchlorate was prepared in a concentrated aqueous solution by neutralizing 60% perchloric acid with solid mercuric oxide. As a small amount of a yellow solid was precipitated, the supernatant of the mixture was pipetted out and standardized by titration against an aqueous potassium thiocyanate solution, using ferric ammonium sulfate as the indicator. Test solutions of mercuric perchlorate in DMF were then prepared from this aqueous solution. The water introduced during this procedure (*ca.* 10 mM) was not removed.

Results

The Standard Potential of Mercury in DMF. In order to evaluate the stability constants of complex ions of mercury(II) by means of polarography, it is necessary to determine the ordinary standard potential($E°$) of the mercury-mercury(II) ion half-cell,[9] which is expressed by the equation:

$$E° = E - (\boldsymbol{R}T/2\boldsymbol{F}) \ln x_0 \qquad (1)$$

where x_0 is the concentration of the simple or the solvated mercury(II) ion on the dropping mercury electrode at the potential E V *vs.* SCE.[10] The value of x_0 can be obtained by:

$$x_0 = {}^*x_0 - i/k_0 \qquad (2)$$

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[1] J. Bjerrum, G. Schwarzenbach and L. G. Sillen, "Stability Constants of Metal-Ion Complexes. Part II. Inorganic Ligands," Spec. Publ. 7, Chem. Soc., London (1958).

[2] G. Ellendt and K. Cruse, *Z. Phys. Chem.*, **201**, 130 (1952).

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

[4] M. Breant and N. V. Kiet, *C. R. Acad. Sci., Paris, Ser. C.*, **262**, 955 (1966).

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

[6] Y. Matsui, Y. Kurosaki and Y. Date, *ibid.*, **43**, 1707 (1970).

[7] Y. Matsui, Y. Kurosaki and Y. Date, *ibid.*, **43**, 2046 (1970).

[8] K. Takaoka, *Rev. Polarography*, **14**, 63 (1966).

[9] C. J. Nyman and G. S. Alberts, *Anal. Chem.*, **32**, 207 (1960).

where $^*x_0$ is the concentration of the mercury(II) ion in the bulk of the solution; i, the cathodic current flowing at the potential E, and k_0, the Ilkovic equation constant for the mercury(II) ion. The constant k_0, which is equal to $i_d/^*x_0$, can be determined by measuring the cathodic diffusion current, i_d, flowing as a result of the reduction of the mercuric perchlorate at a given concentration, $^*x_0$.

Figure 1 shows a polarogram of 0.97 mM mercuric perchlorate obtained in DMF containing 0.1 M tetraethylammonium perchlorate at 25°C. An acute maximum was observed at every concentration of the mercury(II) ion studied. The height of this maximum increased with an increase in the concentration of the depolarizer. It was suppressed only a little by the addition of polyvinyl chloride, which is known to suppress the maxima given by various metal ions in DMF.[6,11] Immediately after the maximum was passed, the current suddenly decreased and reached the plateau of the wave. The height of the plateau was nearly proportional to the concentration of the depolarizer and to the square root of the effective height of the mercury head (Table 1); this indicates that the limiting current is controlled by diffusion.

From these polarographic data, k_0 was calculated to be 3.54×10^{-3} A/M. The value of E° could be determined directly from the polarographic data of the mercuric perchlorate if no maximum wave appeared. In practice, however, the value of E° was calculated from the polarographic data concerning the anodic dissolution of mercury in DMF containing 0.1 M tetraethylammonium perchlorate. The value of E at an arbitrary current of -1 μA was found to be 0.452 ± 0.004 V *vs.* SCE, while the value of E° was calculated from Eqs. (1) and (2) as 0.557 ± 0.004 V *vs.* SCE.

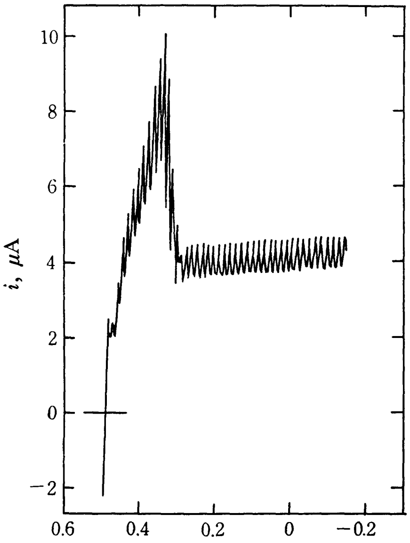

Fig. 1. Polarogram of 0.97 mM mercuric perchlorate in DMF at 25°C.

Table 1. Relation between the limiting current (i_d) of 0.97 mM mercuric perchlorate and pressure on the dropping mercury ($h_{corr.}$)

$h_{corr.}$ (cm)	i_d (μA)	$i_d/(h_{corr.})^{1/2}$
37.3	3.25	0.532
44.3	3.47	0.521
54.3	3.84	0.521
64.3	4.18	0.521
74.3	4.48	0.520

It is remarkable that the standard potential of mercury is more negative in DMF than in water ($E^\circ=0.589$ V *vs.* SCE, obtained in water at an ionic strength of 1.0 M[12]) even though the dielectric constant of DMF is lower than that of water. This indicates that the mercury(II) ion may be strongly solvated in DMF. The specific solvation of the mercury(II) ion by DMF was also suggested by the fact that the diffusion constant of the mercury(II) ion in DMF (3.92×10^{-6} cm^2 sec^{-1} at 25°C), calculated on the basis of the Ilkovic equation, was unusually small compared with that in an aqueous solution (8.2×10^{-6} cm^2 sec^{-1} at 25°C[13]). The solvated mercury(II) ion must be unstable, for it was observed that metallic mercury was separated out from the 0.1 M solution of mercuric perchlorate in DMF when it was left standing at room temperature for a few days. This may be due to the reduction of the mercury(II) ion by one-electron transfer from the solvating DMF molecules.

Evaluation of the Stability Constants of the Tri- and Tetrahalogenomercurate Ions. When the halide ion is added to a 0.1 M solution of tetraethylammonium perchlorate in DMF, two new anodic waves appear. This can be explained in terms of the formation of complexes between the halide ion and the mercury(II) ion.[5-7] The general equation, which relates the potential of the dropping mercury electrode to the current flowing when mercury is oxidized to form complex ions, is:[9]

$$E = E^\circ + (\boldsymbol{R}T/2\boldsymbol{F})\ln(i/k_c) - (\boldsymbol{R}T/2\boldsymbol{F})\ln F_0(x) \qquad (3)$$

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[10] The concentration of the simple mercury(II) ion is, compared with that of the supporting electrolyte, so low that the activity coefficient of the former may be constant; therefore, it was assumed to be equal to one for the sake of simplicity.

[11] S. Musha, T. Wasa and K. Tani, *Rev. Polarography*, **11**, 169 (1963).

[12] C. J. Nyman and E. P. Parry, *Anal. Chem.*, **30**, 1255 (1958).

[13] I. M. Kolthoff and C. S. Miller, *J. Amer. Chem. Soc.*, **63**, 2732 (1941).

where:

$$F_0(x) = 1 + \beta_1 x + \beta_2 x^2 + \cdots + \beta_j x^j \quad (4)$$

In this equation, x represents the concentration o the halide ion at the electrode surface; β_j, the overall stability constant of the complex $HgX_j^{(2-j)}$, and k_c, the Ilkovic equation constant for the complex ions. The value of k_c may vary with different complex ions, but the variation seems to be very slight and so the value was assumed to be constant throughout this series. The value of $F_0(x)$ can be readily obtained at every potential of the waves from Eq. (3), since the other terms in Eq. (3) are experimental quantities.

At the potential corresponding to the more negative of the polarographic waves given by the halide ion, only two halo complexes, *i.e.*, the tri- and tetrahalogenomercurate ions, are formed by the reactions:[7)]

$$Hg + 4X^- \rightleftarrows HgX_4^{2-} + 2e \quad (5)$$

$$Hg + 3X^- \rightleftarrows HgX_3^- + 2e \quad (6)$$

The presence of the other complex ions can be disregarded. Thus,

$$F_0(x) = \beta_3 x^3 + \beta_4 x^4 \quad (7)$$

When K_4 denotes the stepwise stability constant of the tetrahalogenomercurate ion, we obtain:

$$F_0(x) = \beta_3 x^3 (1 + K_4 x)$$

or:

$$\log F_0(x) = \log \beta_3 + 3 \log x + \log(1 + K_4 x) \quad (8)$$

In this equation, x can be expressed by the equation:[7)]

$$x = (k_c/6k_x)[y - r + \{(y+r)^2 + 4ir/k_c\}^{1/2}] \quad (9)$$

where:

$$y = (3i_d - 4i)/k_c$$

$$r = 3k_x/k_c K_4$$

and where k_x is the Ilkovic equation constant for the halide ion. Since the terms on the right side of Eq. (9) are all experimental quantities except for r, which has been roughly estimated for every halide ion in a manner described in a previous paper,[7)] the value of x can be evaluated at every potential of the waves.

Figure 2 is a plot of $\log F_0(x)$ *vs.* $\log x$ for the polarographic data of 1.0 mM tetraethylammonium chloride, where the value of r was taken to be 5×10^{-4} M. As is to be expected from Eq. (8), the plot becomes linear, with a slope of 3.0, in the region where the value of x is small enough for the term of $\log(1 + K_4 x)$ to be disregarded. Thus, the value of $\log \beta_3$, which is approximately equal to $\log F_0(x) - 3\log x$ if the term of $\log(1 + K_4 x)$ is negligible, was calculated to be 31.23. The value of $\log K_4$ was also determined to be 3.34 by the measurement of the deviation of the plot from linearity. The solid curve shown in Fig. 2 was calculated using these values for the stability constants obtained. It seems that the values can adequately account for the polarographic data.

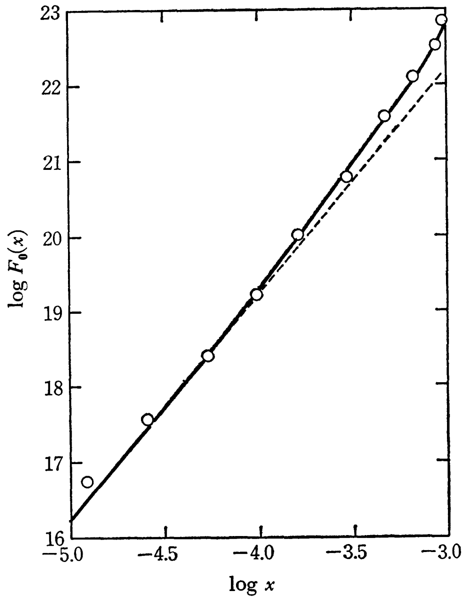

Fig. 2. Plot of $\log F_0(x)$ *vs.* $\log x$ for the more negative wave of the chloride ion.
The solid line was calculated with the stability constants in Table 2.

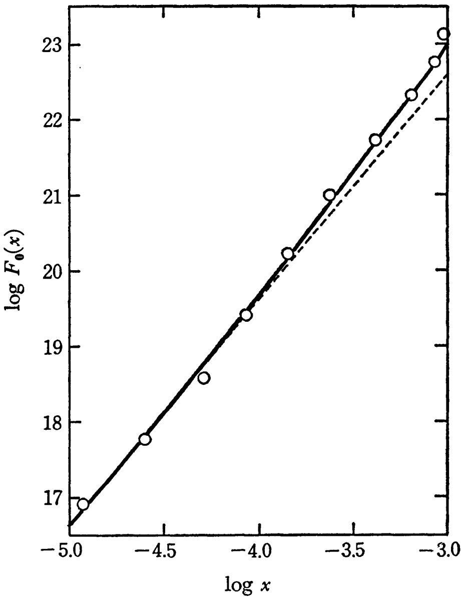

Fig. 3. Plot of $\log F_0(x)$ *vs.* $\log x$ for the more negative wave of the bromide ion.
The solid line was calculated with the stability constants in Table 2.

A similar procedure was applied to the more negative of the waves given by a 1.0-mM solution of tetraethylammonium bromide or iodide in DMF.

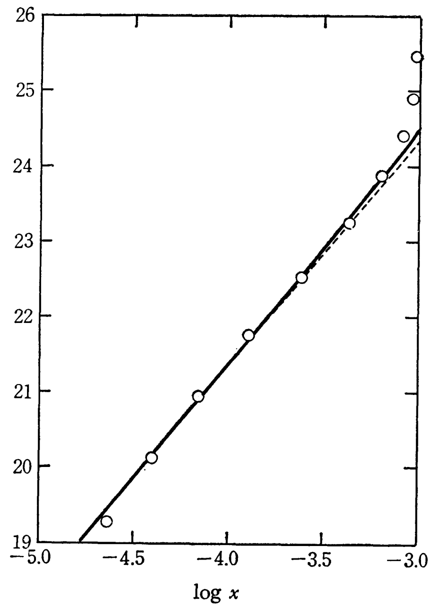

Fig. 4. Plot of log $F_0(x)$ *vs.* log x for the more negative wave of the iodide ion.
The solid line was calculated with the stability constants in Table 2.

TABLE 2. STABILITY CONSTANTS OF THE HALO COMPLEXES OF MERCURY(II) IN DMF CONTAINING 0.1 M TETRAETHYLAMMONIUM PERCHLORATE AT 25°C

Ligand	log β_2	log K_3	log β_3	log K_4	log β_4
Cl^-	24.16	7.07	31.23	3.34	34.57
Br^-	24.17	7.45	31.62	3.11	34.73
I^-	25.93	7.41	33.34	2.68	36.02

The variation in log $F_0(x)$ with the log x value is shown in Fig. 3 for the bromide ion (r is taken as 1×10^{-3} M) and in Fig. 4 for the iodide ion (r is taken as 1×10^{-2} M). All the values of β_3, K_4, and β_4 obtained are given in Table 2. Every plot of log $F_0(x)$ *vs.* log x was found to deviate from the calculated solid curve, especially in the case of the iodide ion, in the potential range where the anodic current begins to flow. This may be due to the adsorption of the depolarizers on the electrode surface, as has previously been descrived.[6)]

Evaluation of the Stability Constant of Mercuric Halide. The overall stability constant of mercuric halide can be determined more easily than those of the tri- and tetrahalogenomercurate ions. As has been described in previous papers[5-7)] the more positive of the polarographic waves given by the halide ion in DMF is due to the reversible oxidation of mercury to mercuric halide. Since the concentrations of the halide ion and the tetrahalogenomercurate ion at the electrode surface become negligible at the potential corresponding to the plateau of the more negative wave, the electrode reaction at the more positive wave can be simply expressed by the equation:

$$Hg + 2HgX_3^- \rightleftarrows 3HgX_2 + 2e \qquad (10)$$

Therefore, the potential of the dropping mercury electrode at any point of this wave should be given by:

$$E = E^\circ + (\boldsymbol{RT}/2\boldsymbol{F})\ln(\beta_3^2/\beta_2^3) + (\boldsymbol{RT}/2\boldsymbol{F})\ln(x_2^3/x_3^2) \qquad (11)$$

where x_2 and x_3 are the concentrations of mercuric halide and the trihalogenomercurate ion respectively at the electrode surface. x_2 and x_3 are expressed by:

$$x_2 = 3(i-i_d)/k_c \qquad (12)$$

$$x_3 = 2(i_d'-i)/k_c \qquad (13)$$

where the current flowing at any point of the wave (i), as well as the diffusion current of the first and second anodic waves (i_d and i_d' respectively), is measured on the basis of the total anodic current. By introducing Eqs. (12) and (13) into Eq. (11) and by rearranging the resulting equation, we obtain:

$$\log\beta_2 = (1/3)\{2\boldsymbol{F}(E^\circ-E)/2.303\boldsymbol{RT} + 2\log\beta_3 + \log(27/4k_c) + \log(i-i_d)^3/(i_d'-i)^2\} \qquad (14)$$

Since the terms on the right side are either experimental quantities or known ones, the value of log β_2 can be readily calculated at any potential of the wave. As an example, the results of the calculation for the wave given by the bromide ion are given in Table 3. The mean values of log β_2 thus obtained for various halides are given in Table 2.

TABLE 3. LOG β_2 CALCULATED AT VARIOUS POTENTIALS IN THE MORE POSITIVE WAVE OF THE BROMIDE ION

E (V *vs.* SCE)	i (μA)*	log β_2
0.056	2.31	24.19
0.081	2.34	24.13
0.106	2.37	23.99
0.131	2.54	24.19
0.156	2.72	24.21
0.181	2.87	24.19
0.206	3.02	24.21
0.231	3.10	24.22

* $i_d = 2.26\,\mu$A and $i_d' = 3.16\,\mu$A.

Discussion

Among the stability constants obtained in this work, only that of the tetrahalogenomercurate ion can be compared with those in earlier works, since the other constants in DMF have never been reported. Given and Peover[3)] have determined the value of log β_4 to be about 30 for $HgCl_4^{2-}$ in DMF containing 1.0 M lithium perchlorate, and to be 38.79 for HgI_4^{2-} in DMF containing 0.1 M lithium perchlorate, by means of polarography at

20°C. Their procedure for determining the constants requires the measurement of the potential of the dropping mercury electrode, at an arbitrary current of $-1.0\ \mu$A, as a function of the concentration of the halide ion. In using this method, the concentration of the complexing agent in the bulk of the solution must be high enough to be effectively equal to that on the electrode surface when any slight current is flowing. Consequently, only the overall stability constant of the highest complex ion of mercury(II) can be evaluated by this procedure. Moreover, in applying this method we must pay attention to the possibility that the potential of the dropping mercury electrode at $-1\ \mu$A can be shifted in a more negative direction by the adsorption of the depolarizer. Breant and Kiet,[4] using the same method as Given and Peover, also determined the values of log β_4 to be 32.9 for $HgCl_4^{2-}$, 35.2 for $HgBr_4^{2-}$, and 36.6 for HgI_4^{2-} in DMF containing 0.1 M perchloric acid. The values presented by them agree approximately with those in the present work, although the two sets of experimental conditions are not quite the same.

It is well known that the stabilities of the halo complexes of such metallic ions as Cu(I), Ag(I), Cd(II), and Hg(II), whose electronic configurations are representative of pseudo-inert gas ($s^2p^6d^{10}$), as opposed to those whose electronic configurations are representative of noble gas (s^2p^6), increase in an aqueous solution in the following order:

$$F^- < Cl^- < Br^- < I^-$$

This has been explained in terms of the mutual polarization of the metallic ions and ligands. The results in Table 2 show that the alteration in the stability of the complex ions with the ligands in DMF follows the same sequence as that in an aqueous solution (Table 4[1]), although the former is not so great as the latter. The difference in electronegativity between mercury and halogen ($\Delta\chi_{Hg-F}=2.1$, $\Delta\chi_{Hg-Cl}=1.1$, $\Delta\chi_{Hg-Br}=0.9$, and $\Delta\chi_{Hg-I}=0.6$[14]) indicates that all the bonds of Hg–Cl, Hg–Br, and Hg–I are rich in covalent character, and that this covalent character decreases and the ionic character increases in the following sequence:

$$\text{Hg-I} < \text{Hg-Br} < \text{Hg-Cl} < \text{Hg-F}$$

However, no such difference in bond character among them can be clearly observed in DMF. This may be due to the low dielectric constant of DMF (37.8[11]). On the other hand, the dielectric constant of water (78.54) may be high enough to distinguish the difference in bond character.

TABLE 4. STABILITY CONSTANTS OF THE HALO COMPLEXES OF MERCURY(II) IN WATER CONTAINING 0.5 M SODIUM PERCHLORATE AT 25°C*

Ligand	log β_2	log K_3	log β_3	log K_4	log β_4
Cl^-	13.22	0.85	14.07	1.00	15.07
Br^-	17.33	2.41	19.74	1.26	21.00
I^-	23.82	3.78	27.60	2.23	29.83

* Ref. 1.

It is interesting that the values of K_4 of $HgCl_4^{2-}$, $HgBr_4^{2-}$, and HgI_4^{2-} decrease in this order. This may be related to the difference in the ionic radii of the halide ions. As has been described above, the bond between mercury and iodine is essentially covalent in character. As the value of β_3 of HgI_3^- is very large, it may be considered that each covalent Hg–I bond in HgI_3^- is readily formed without any steric hindrance from the other iodide ions. The formation of the fourth Hg–I bond, on the other hand, may be sterically hindered by the other three iodide ions already combined with the mercury(II) ion. Probably as a result, the K_4 value of HgI_4^{2-} becomes very small. As the ionic radii of I^-, Br^-, and Cl^- decrease in this order, the stepwise stability constants increase in that sequence. No such steric hindrance can be observed in an aqueous solution (Table 4), probably because, in water, the effect of the difference in bond character among Hg–Cl, Hg–Br, and Hg–I on the stability constant becomes larger than the steric effect.

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14) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca (1960), p. 93.