307. Polarography of Iodide and Chloride Ions in Dimethylformamide.

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Polarograms of iodide or chloride ion with a dropping mercury electrode in dimethylformamide show two anodic waves, of which that at the more negative potential is due to the oxidation of mercury to the tetrahalogenomercurate ion. The waves become cathodic on addition of mercuric perchlorate. The overall equilibrium constant for the reaction $Hg^{2+} + 4I^- \rightleftharpoons HgI_4^{2-}$ is approximately $6{\cdot}2 \times 10^{38}$ at 20° in 0·1M-lithium perchlorate. Mercurous chloride is soluble in solutions of lithium chloride in dimethylformamide. The use of a mercury pool anode as a reference electrode in polarography in halide–dimethylformamide solutions is discussed in the light of these results.

Various polarographic studies [1-5] have indicated that the potential of a mercury anode under a solution of tetra-alkylammonium iodide in dimethylformamide (and probably also in dioxan–water, acetonitrile, and Methyl Cellosolve) assumes a well-regulated value, suitable for reference purposes. This potential is in each case some 0·5 v negative to an aqueous saturated calomel electrode. We report here experiments designed to elucidate some features of the chemistry of mercury relating to these facts. A note describing some of the results has appeared.[6]

Experimental

Dimethylformamide was as received from Griffin and George; the water content (Karl Fischer) was about 0·01%. Tetraethylammonium iodide was prepared as described previously.[2] Other materials were " AnalaR " if available, or otherwise a good laboratory grade. However, mercuric perchlorate was used as a concentrated aqueous solution, made by neutralising 60% perchloric acid with solid mercuric oxide. A Tinsley polarograph, model 14/3, was used for the polarographic measurements. An H-cell was used for polarography; the bridge liquid, separated from the calomel and polarographic cells by No. 4 porosity sintered-glass discs, consisted of 1·0N-aqueous lithium perchlorate, and the base solution for polarography was a 0·1N-solution of the same salt in dimethylformamide. In some experiments the bridge solution was made up in dimethylformamide instead of water. This was found to be unsatisfactory because potassium chloride from the calomel cell crystallised on the sinter in the organic solvent; this made the cell resistance and measured potentials variable. All the results were corrected for *iR* drop. The anode-to-cathode resistance was 1500—4000 ohms.

Conductivities were measured with a Mullard conductivity bridge, operated at 3kc./sec., and blacked platinum electrodes.

Results.—(a) *Solubility relations*. Mercuric chloride, iodide, and perchlorate, lithium chloride and perchlorate, and a number of tetra-alkylammonium salts were easily soluble in dimethylformamide, and mercurous chloride and iodide are insoluble (mercuric iodide is extremely soluble: *ca.* 4M at 20°). A solution of mercuric chloride in dimethylformamide shaken with mercury at once precipitates the mercurous compound, but if 0·1N-lithium chloride or tetraethylammonium iodide is present, no precipitation occurs. If calomel is shaken with lithium chloride solution for some while, it dissolves and mercury separates; on dilution with water the solution gives positive reactions for Hg^{II} (H_2S, dithizone). Lithium perchlorate does not prevent separation of calomel from a solution of mercuric chloride containing mercury. There is little separation of mercurous iodide when a solution of the mercuric salt in dimethylformamide is shaken with mercury.

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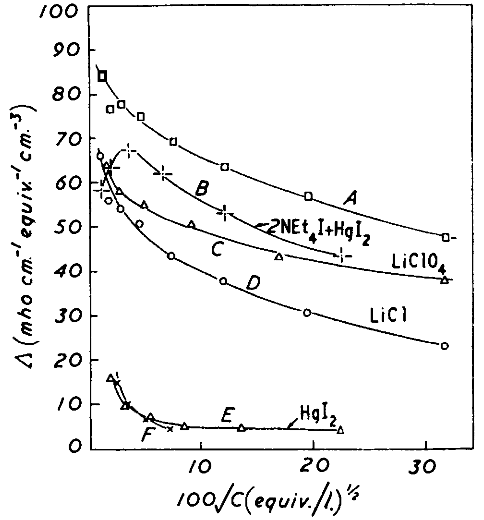
[1] Hoijtink, van Schooten, de Boer, and Aalbersberg, *Rec. Trav. chim.*, 1954, **73**, 355.
[2] Given, Peover, and Schoen, *J.*, 1958, 2674.
[3] Wawzonek, Blaha, Berkey, and Runner, *J. Electrochem. Soc.*, 1955, **102**, 235.
[4] Bergmann, *Trans. Faraday Soc.*, 1954, **50**, 829; 1956, **52**, 690.
[5] Given, *J.*, 1958, 2685.
[6] Given and Peover, *Nature*, 1958, **182**, 1226.

(b) *Conductivities.* A few approximate measurements of the conductivity of solutions of some salts in dimethylformamide have been made, to test the ionisation of mercuric compounds in this medium. The equivalent conductivities at room temperature (about 20°) are plotted in Fig. 1, together with those of the supporting electrolytes for comparison; the conductivity of a mixture of tetraethylammonium iodide and mercuric iodide of mole-ratio 2 : 1 is also shown.

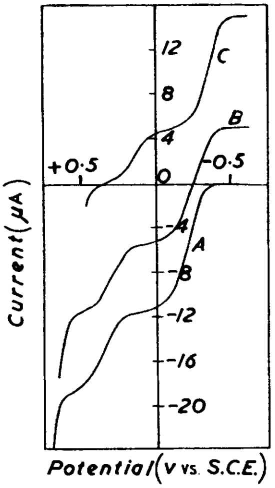
(c) *Polarographic measurements.* The nature of the reactions of mercury in the polarographic cell has been investigated by studying the polarography of lithium chloride and tetraethylammonium iodide in 0·1N-lithium perchlorate as supporting electrolyte, with and without added mercuric ions. A similar study of these system in aqueous solutions has been made by Kolthoff and Miller,[7] and we followed their methods.

FIG. 1. *Equivalent conductivities of salts in dimethylformamide.*



A, NEt$_4$I. *B*, Conductivity and concentration of the mixture 2NEt$_4$I + HgI$_2$, calculated on the basis of complete association to (NEt$_4$)$_2$HgI$_4$. *C*, LiClO$_4$. *D*, LiCl. *E*, HgI$_2$. *F*, HgCl$_2$.

FIG. 2. *Polarography of tetraethylammonium iodide in* 0·1M-*lithium perchlorate.*



A, 4·76mM. *B*, 4·76mM-NEt$_4$I + 0·7mM-Hg(ClO$_4$)$_2$. *C*, 4·76mM-NEt$_4$I + 2·1mM-Hg(ClO$_4$)$_2$.

Lithium perchlorate by itself gave a " dissolution wave," that is, the current increased without limit as the potential of the dropping mercury electrode become more positive (above +0·4 v). Perchlorates in aqueous solutions give a similar wave,[6] owing to the reaction $2Hg \longrightarrow Hg_2^{2+} + 2e$, and the equation of the wave is $E_{de} = E_{Hg}^{\circ} + (\boldsymbol{RT/2F}) \ln i$. Plots of E_{de} against log *i* for lithium perchlorate in dimethylformamide gave fairly good straight lines of slopes 0·03—0·045 v (this type of plot is exceptionally sensitive to errors in the measurement of potential and the correction for *iR* drop).

TABLE 1. *Polarography of iodide and chloride ions in* 0·1N-*lithium perchlorate in dimethylformamide.*

Salt	Concn. (mM)	$E_{\frac{1}{2}}$ (v *vs.* S.C.E.)	*I*	Temp.
LiCl	2·52	−0·17, +0·125	1·17, 0·52	19·5°
NEt$_4$I	1·96	−0·32, +0·10	1·24, 0·50	20

Lithium chloride and tetraethylammonium iodide in 0·1N-lithium perchlorate both give two oxidation waves (see example in Fig. 2, *A*), whose half-wave potentials and wave heights, I ($= i_d/cm^{\frac{2}{3}}t^{\frac{1}{6}}$), are given in Table 1. The wave heights were effectively constant in the concentration range 1—5mM; average values are given in Table 1.

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[7] Kolthoff and Miller, *J. Amer. Chem. Soc.*, 1941, **63**, 1403.

In the analysis of the waves of complex mercury ions used by Kolthoff and Miller [7] one writes the electrode reaction as:

$$Hg + aX^- \rightleftharpoons HgX_a^{(a-2)-} + 2e \quad . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

The potential of the dropping electrode is given by:

$$E_{de} = C + (\boldsymbol{RT}/2\boldsymbol{F}) \ln [Hg^{2+}] \quad . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

where $[Hg^{2+}] = K[HgX_a^{(a-2)-}]/[X^-]^a$ and C is a constant.

It can easily be shown that the equation of the wave is

$$E_{de} = C' + (\boldsymbol{RT}/2\boldsymbol{F}) \ln [i/(i_d - i)^a] \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

Hence one plots E_{de} against the logarithmic function for various values of a, to determine the value that gives a straight line of slope $\boldsymbol{R}T/2\boldsymbol{F}$. A plot of E_{de} against $\log i/(i_d - i)^4$ for the more negative iodide wave gives a good straight line of slope 0·029 (see Fig. 3), and the electrode reaction is therefore:

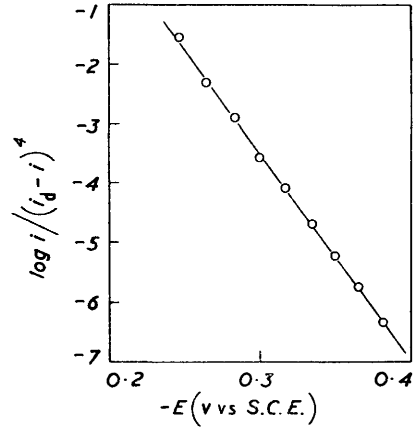


Fig. 3. *Logarithmic analysis of more negative wave of* 4·76mM-*tetraethylammonium iodide in* 1·0M-*lithium perchlorate–dimethylformamide* (*slope* 0·029v).

$$Hg + 4I^- \rightleftharpoons HgI_4^{2-} + 2e \quad . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

The corresponding plot for the more negative chloride wave was linear with about the required slope over the greater part of its length but became curved at less negative values of E_{de}, suggesting complication by a further reaction:

$$HgCl_4^{2-} \rightleftharpoons HgCl_3^- + Cl^- \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

Equation (3) shows that the half-wave potentials should be concentration-dependent:

$$E_{\frac{1}{2}} = C'' - (3\boldsymbol{R}T/2\boldsymbol{F}) \ln i_d \quad . \ . \ . \ . \ . \ . \ . \ . \quad (6)$$

that is, a ten-fold increase in concentration should shift $E_{\frac{1}{2}}$ to more negative potentials by 0·09 v. In the range of concentrations studied (1—5 mM) the shift appeared to be less than would correspond with this for the iodide wave and more for the chloride wave.

For reasons set out in the Discussion Kolthoff and Miller's analysis cannot be applied to the more positive halide waves and we have not succeeded in identifying the electrode reactions. The unexpected observation was made that the half-wave potential of the iodide wave became more *positive* with increasing concentration.

As increasing amounts of mercuric perchlorate were added to solutions of lithium perchlorate containing definite amounts of a halide ion both waves became cathodic and finally with sufficient Hg^{2+} the " dissolution wave " became partly cathodic (see Fig. 2, *B* and *C*); at the same time the waves decreased somewhat in height, which is consistent with the lower diffusion coefficient of the complex ions compared with ligand. The shape of the more negative waves, and in 1·95mM-iodide and 3·7mM-chloride the half-wave potentials, was unchanged by additions of mercuric perchlorate up to 2mM. In 4·76mM-iodide there was an appreciable shift of both half-wave potentials to more negative voltages as mercuric ion was added. We do not attempt to correlate the ratio of cathodic to anodic parts of the wave with amount of mercuric perchlorate added, since the concentration of the latter, owing to its method of preparation, was not known accurately.

(d) *Stability constants of complex mercuric ions.* The standard procedure [8] for determining polarographically the stability constants of complex metal ions cannot be applied to the oxidation waves of mercury complexes,[9] and special procedures have to be used. We followed the method used by Nyman, Roe, and Masson [9] in their study of ethylenediamine complexes of mercury. This requires the measurement, not of half-wave potentials, but of the potential at which the current is 1 μA more negative than the residual current. If the potentials, defined in this way, are E'_s and E'_c for the simple and complex ions respectively, then

$$E'_c = E'_s - (\boldsymbol{RT}/n\boldsymbol{F}) \ln \beta_a (Cf_{X^-})^a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where β_a is the overall equilibrium constant of the formation of the complex HgX_a, and C is the concentration and $f_{x'}$ the activity coefficient of the complexing agent; it is assumed in this equation that the ratio of the square roots of the diffusion coefficients of complex ion to ligand is unity. In using this method the concentration of complexing agent must be high enough for the concentration on the electrode surface to be effectively equal to that in the bulk of the liquid. For a complex HgX_4^{2-} eqn. (7) can be rewritten:

$$E'_s - E'_c = (\boldsymbol{RT}/2\boldsymbol{F}) \ln \beta_4 + (2\boldsymbol{RT}/\boldsymbol{F}) \ln f_{X^-} + (2\boldsymbol{RT}/\boldsymbol{F}) \ln C \quad . \quad . \quad . \quad (8)$$

Thus in a solution of constant ionic strength, where f_{X^-} will be constant, a plot of $E'_s - E'_c$ against log C should give a straight line of slope 0·116 at 20°. Since the potential, E''_s, measured on the dissolution wave refers to mercurous ion, it is necessary, in order to obtain E'_s, to add to E''_s the difference between the standard electrode potentials of the mercury–mercuric and mercury–mercurous couples (0·06 v).

FIG. 4. *Difference in potentials of simple and complex mercuric ions as a function of concentration of tetraethylammonium iodide* (*slope* 0·116v).

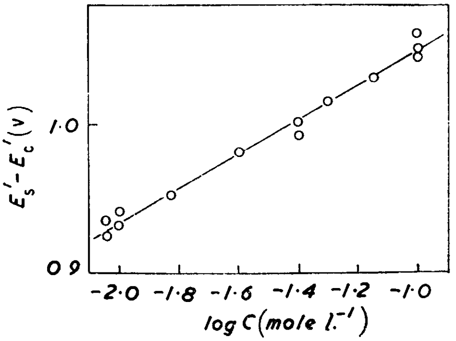
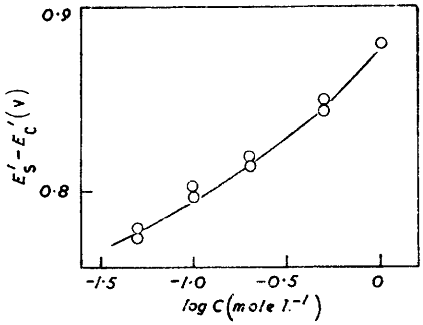


FIG. 5. *Difference in potentials of simple and complex mercuric ions as a function of concentration of lithium chloride.*



We have measured the potentials, E'_c and E''_s, for tetraethylammonium iodide solutions of concentration 0·01—0·1M at 20°, keeping the total ionic strength at 0·1M by additions of lithium perchlorate. The results are shown in Fig. 4; it is seen that a good straight line of the theoretical slope for the HgI_4^{2-} complex is obtained. From the intercept at $C = 1$, we obtain the product $\beta_4 f_{I^-}{}^4 = 6{\cdot}5 \times 10^{38}$ for a total ionic strength of 0·1M at 20°. A few similar measurements were made for chloride ion in the range 1—0·04M, the total ionic strength being kept at 1·0M by additions of lithium perchlorate, with results shown in Fig. 5. Here a curve is obtained showing that appreciable amounts of more than one complex exist at equilibrium at these concentrations. The tangent to the curve at log $C = 0$ has approximately the slope required for the $HgCl_4^{2-}$ complex.

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[8] Kolthoff and Lingane, " Polarography," Interscience, New York, 2nd Edn. 1952, p. 211 *et seq.*
[9] Nyman, Roe, and Masson, *J. Amer. Chem. Soc.*, 1955, **77**, 4191.

Overall thermodynamic equilibrium constants for the formation of the mercuric complexes were calculated from the above data by the graphical method of de Ford and Hume;[10] this in effect uses extrapolation to zero concentration of complex, so that knowledge of activity coefficients is unnecessary. The data permitted calculation of β_2, β_3, and β_4 for iodide complexes and an approximate value of β_4 for the chloride case (see Table 2).

DISCUSSION

The very high solubility of mercuric iodide suggested the possibility of autocomplex formation, one or both ions perhaps being solvated. However the low degree of ionisation shown by the conductivity measurements argues against this. The data for none of the salts fit the Onsager equation, and plots of Λ_0 against $1/\Lambda$ (not shown) demonstrate that the Ostwald equation is not obeyed. These deviations, indicating ion-pair formation and higher degrees of ionic association, seem suprising in a solvent of fairly high dielectric constant (36·7 at 25°). The decrease in conductivity of the mixture of mercuric and tetraethylammonium iodides at low concentration suggests that dissociation of the HgI_4^{2-} complex to a lower complex occurs in very dilute solution.

The solubility relations among the chlorides of mercury evidently differ in dimethylformamide. The behaviour in the presence of excess of chloride depends on the equilibrium:

$$Hg_2Cl_2(s) + Cl^- \rightleftharpoons Hg(l) + HgCl_3^-$$

(or the corresponding reaction involving $HgCl_4^{2-}$). The observations recorded above show that the equilibrium lies much further to the right in dimethylformamide than in water and the potential of a mercury pool in chloride–dimethylformamide solution cannot be determined by the calomel equilibrium:

$$2Hg + 2Cl^- \rightleftharpoons Hg_2Cl_2(s) + 2e$$

The polarographic characteristics of the more negative iodide wave show that in polarography with iodide supporting electrolyte and a mercury pool as anode the metal goes into solution, yielding HgI_4^{2-} ions. Thus the potential of the anode is determined by the oxidation–reduction system of reaction (4); its value remains constant presumably because stable complex formation maintains a concentration of mercury ions in the anode layer sufficiently high to ensure that further quantities, produced by electrolysis, do not increase it by a significant fraction. The similarity of the half-wave potentials of hydrocarbons with iodide supporting electrolyte in dimethylformamide, 75% and 96% dioxan–water, acetonitrile, and Methyl Cellosolve (see ref. 5) creates the presumption that the pool potential is similar in all these media and therefore that the same equilibrium determines it.

TABLE 2. *Equilibrium constants of formation of complex mercuric ions (data for systems in water and acetonitrile taken from ref.* 12).

Ligand	Medium	$\log K_3$	$\log K_4$	$\log \beta_4$	$\log K_3K_4$
Cl^-	0·5M-$NaClO_4$–H_2O	0·95	1·05	15·22	2·0
Cl^-	CH_3·CN	6·0	2·23	—	8·23
Cl^-	1·0M-$LiClO_4$–DMF *	—	—	*ca.* 30	—
I^-	0·5M-$NaClO_4$–H_2O	3·67	2·37	29·86	6·04
I^-	CH_3·CN	5·95	1·61	—	7·56
I^-	0·1M-$LiClO_4$–DMF *	4—5	2·79	38·79	*ca.* 7

* DMF = Dimethylformamide: measurements made at 20°.

We have found that a mercury pool used as anode in perchlorate does not provide a stable reference potential; for example the first half-wave potential of anthraquinone is concentration-dependent in perchlorate solution but not in iodide or chloride. The potential of the pool in 0·1M-lithium perchlorate is about −0·28 v *vs.* S.C.E. and +0·3 v *vs.* mercury pool in 0·1M-tetraethylammonium iodide. Brown and Al-Urfali[11] have reported

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[10] de Ford and Hume, *ibid.*, 1951, **73**, 5321.

[11] Brown and Al-Urfali, *J. Amer. Chem. Soc.*, 1958, **80**, 2113.

[12] Stability Constants of Metal-ion Complexes. Part II. Chem. Soc. Special Publ. No. 7, 1958.

the half-wave potentials of a number of metal ions each at a single concentration in dimethylformamide, referred to the potential of the pool. For some ions they used an iodide as supporting electrolyte and for others a perchlorate; they appear not to have appreciated that the reference potentials are considerably different in these media or to have considered their stability.

The stability constants of the complex mercury ions are higher (in the case of chloride as ligand, much higher) in dimethylformamide than they are in water. Some comparative figures for solutions in water and in acetonitrile (in which the constants are also higher than they are in water) are collected in Table 2; the notation used is that of the source of the data,[12] that is, the β's are overall constants, and the K's refer to addition of one ion of ligand.

It is primarily these differences in stability constants that cause much of the familiar solution chemistry of mercury to be considerably changed if dimethylformamide is used as solvent.

It is noteworthy that the pool potential in 0·1N-tetraethylammonium iodide and in 1·0N-lithium chloride in dimethylformamide is close to the electrocapillary maximum of mercury.[2] Consequently the drop-time is the same whether the electrodes are in open or short circuit.

We suggest that the more positive wave given by both halides arises as follows. As the potential of the dropping electrode is made more positive starting from, say, —0·4 v, mercury goes into solution by reaction with halide ions. At the more positive end of the first wave the halide concentration on the drop is zero, and all halide ions arriving at it by diffusion react to give HgX_4^{2-} (which in the case of chloride may dissociate to some extent to $HgCl_3^-$). However, at a sufficiently positive potential, the oxidation of mercury to another complex, perhaps HgX_3^-, becomes possible, and as the potential traverses this second wave the ratio HgX_3^-/HgX_4^{2-} on the drop increases until at the more positive end all the halide reacts to give the second complex only. The shape of the wave is therefore governed by *two* equilibria, the stationary concentration of halide on the drop being zero throughout. We have not succeeded in setting up the equation of this complex wave; the suggestion that it characterises oxidation to trihalogenomercurate is plausible but not proved.

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