

high, because the hydroxide is not fully hydrated in crystalline lithium hydroxide monohydrate. A further problem is that the experimental values for the autoprotolysis ratio, $K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}}$, refer to dilute solutions, whereas the spectroscopic data for the hydronium ion in water refers to concentrated solutions of acid. Thus the hydronium ion in these solutions may not be fully hydrated; if this is so then the stretching frequency for H_3O^+ should be lower than 2900 cm.^{-1} , the value used in our calculations.

The comparatively poor agreement between the experimental and calculated values for the isotope effects on water autoprotolysis would be much improved by the choice of slightly lower values for the stretching frequencies of the hydroxide and hydronium ions. Such changes will have less effect upon the calculations for dissociations of acids other than water, because we relate their frequencies to those of water and its ions. Therefore the effect of anticipated future changes in the frequencies assigned to water and its ions will be partially self-cancelling in all of our calculations except for the autoprotolysis equilibrium.

Further improvement in this type of calculation will depend on the observation of more hydrogen bond stretching frequencies for different solvated acids and bases. This pertains particularly to the

extension of the method to acids and bases containing nitrogen and other electronegative atoms. However, even for acid-base equilibria in which the relevant frequencies are not known, or cannot be estimated, it is possible to predict the direction of changes in the ratio $K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}}$ with changes in the dissociation constants and the effect of changing the number of equivalent ionizable, hydrogen atoms in the acid. One major limitation which will be difficult to surmount is the neglect of the bending frequency changes. This seems to impose some absolute limit on the possible refinement of the method as the detailed accounting of these frequencies for any large number of examples would be extremely difficult, although we have shown this neglect not to be serious in the calculations relating to the autoprotolysis of water.

Acknowledgments.—The authors appreciate many helpful discussions of this topic with their colleagues at University College including especially Professors Sir Christopher Ingold, F.R.S.; E. D. Hughes, F.R.S.; D. P. Craig and Drs. J. H. Colloman, D. J. Millen, Y. Pocker and J. H. Ridd. We are also indebted to Professor F. A. Long for valuable criticisms. One of us (V. J. S.) is especially grateful for the hospitality shown to him by the Chemistry Department of U.C.L. during the tenure of his sabbatical leave there.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA]

Effects on Polarographic Waves of the Formation of Insoluble Films on Dropping Mercury¹

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The formation of films of insoluble substances on the surface of dropping mercury may exert two different effects on polarograms: suppression of maxima and alteration of the characteristics of polarographic waves. Considerably less than a monomolecular film of mercurous iodide completely suppresses maxima of both the first and the second kind. Experimental results presented in this paper show that the mercurous iodide film behaves like an anionic surface-active organic compound in regard to its effect on the characteristics of polarographic waves. The film makes the reduction wave of aquo-copper(II) ions more reversible, while that of oxygen is made more irreversible. The reduction of persulfate is strongly inhibited in the potential range where the mercurous iodide film is formed.

It is well known that the addition of small amounts of surface-active organic compounds suppresses polarographic maxima, while those substances often change the shape of polarograms. Similar effects are observed when a film of insoluble substances is formed on the dropping mercury.

Lingane² reported that the maximum on the reduction wave of lead ions in $0.1 M$ potassium chloride is completely suppressed when the solution is made $0.001 M$ with respect to iodide ions but gave no interpretation. We found that even at a much smaller concentration of iodide, *e.g.*, $10^{-5} M$, complete suppression of maxima is observed, not only of lead but also of oxygen, copper(II), mercury(II), iron(III) and persulfate, while in the same supporting electrolytes pronounced

maxima were observed in the absence of the trace of iodide. Iodide is effective in suppressing maxima only in the potential range where mercurous iodide is formed anodically. From this experimental fact as well as from characteristics of electrocapillary curves and anodic iodide waves at both the conventional and the rotating dropping mercury electrode, it is concluded that the maximum suppression effect of iodide is due to the formation of a film of mercurous iodide. Bromide and chloride ions also form a film of their mercurous salts and suppress maxima in the potential range where these films are formed. Small amounts of a phenylmercuric salt are also effective in suppressing maxima in the potential range where this substance is reduced to form insoluble diphenylmercury.^{3,4} Effects of the films on the characteristics of the reduction waves of persulfate,

(1) This investigation was supported by a research grant from the National Science Foundation.

(2) J. J. Lingane, Ph.D. Thesis, University of Minnesota, 1938; I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1952, p. 166.

(3) R. Benesch and R. E. Benesch, *THIS JOURNAL*, **73**, 3391 (1951); *J. Phys. Chem.*, **56**, 648 (1952).

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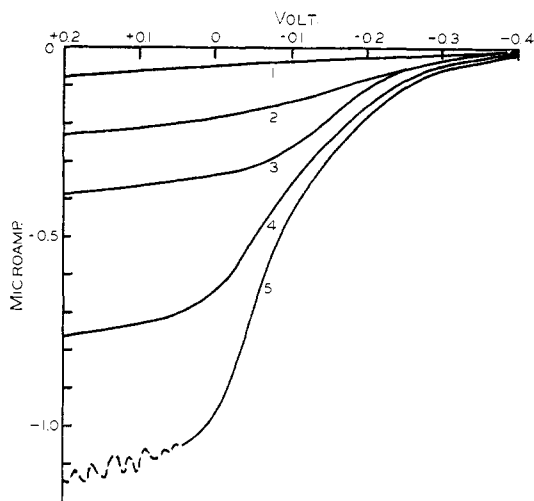


Fig. 1.—Anodic iodide waves at d.m.e. ($h = 44$ cm.) in $0.1 M HClO_4$. Concentration of iodide: 1, 0; 2, $5 \times 10^{-5} M$; 3, $10^{-4} M$; 4, $2 \times 10^{-4} M$; 5, $3 \times 10^{-4} M$.

oxygen and copper(II) and of the anodic copper amalgam wave also are described in this paper.

Experimental

Materials.—All chemicals were C. p. grade and used without further purification. Polyacrylamide (PAA 75) was a product of American Cyanamid Co., New York. Triton X-100 ($C_8H_{17}(C_6H_4)(OCH_2CH_2)_9OH$) was obtained from Rohm and Haas Co., Philadelphia, Pa. Deaeration was done by passing high purity Linde nitrogen.

Electrodes.—The conventional dropping mercury electrode used had these characteristics in $0.1 M$ perchloric acid: $m = 1.32$ mg./sec., $t = 5.06$ sec. (open circuit) at $h = 51.5$ cm. The rotating dropping mercury electrode was of the type described in a previous paper⁵ and rotated at 210 r.p.m. The m and t values in $0.1 M$ perchloric acid were 8.47 mg./sec. and 4.43 sec. (open circuit) at $h = 41.5$ cm., respectively. The cell for the preparation of copper amalgam had a capacity of 200 ml. and was of a type similar to the one described by Delahay⁶ except that a platinum foil was used as anode which was placed in a compartment separated by a sintered glass disk. The copper amalgam was prepared by electrolyzing copper perchlorate in $0.1 M$ perchloric acid. The drop time of the amalgam electrode was 5.50 sec. at $h = 50$ cm. in $0.1 M$ perchloric acid at open circuit.

The reference electrode was a saturated calomel electrode in all experiments.

Measurements.—Polarograms were recorded with a Sargent Polarograph Model XXI. Currents for the wave analysis were measured by operating the instrument manually. Experiments were carried out in a thermostat maintained at $25 \pm 0.1^\circ$.

Experimental Results

Anodic Iodide Waves.—Some evidence is found in the literature of halide film formation on a mercury surface.⁷⁻⁹ If such films are sufficiently strongly adsorbed, a prewave is expected to occur before the main anodic halide wave which would correspond to the formation of a monomolecular layer of the mercurous halide. In order to find whether there is indication of the occurrence of such an adsorption wave, a detailed study was made of the shape of the anodic iodide wave both at the

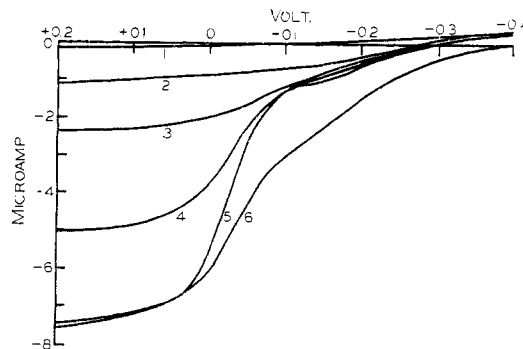


Fig. 2.—Anodic iodide waves at r.d.m.e. in $0.1 M HClO_4$; curves 1–5 were taken at $h = 41.5$ cm., and curve 6 at $h = 81.5$ cm. Concentration of iodide: 1, 0; 2, $2 \times 10^{-5} M$; 3, $5 \times 10^{-5} M$; 4, $10^{-4} M$; 5 and 6, $1.5 \times 10^{-4} M$.

conventional dropping mercury electrode (d.m.e.) and at the rotating dropping mercury electrode (r.d.m.e.).

Figure 1 shows current-potential curves of iodide at the d.m.e. in $0.1 M$ perchloric acid. At iodide concentrations greater than $2 \times 10^{-4} M$ there appears a very slight indication of the occurrence of two waves, while at iodide concentrations smaller than $10^{-4} M$ a well-defined single wave is observed. When the iodide concentration is made greater than $4 \times 10^{-4} M$, current becomes irregular, which was observed also by Kolthoff and Miller⁸ who attributed the irregularity to the formation of a precipitate of mercurous iodide on the mercury surface. At the r.d.m.e., on the other hand, prewaves were much more clearly developed than at the d.m.e. as shown in Fig. 2. This prewave has the typical characteristics of an adsorption wave; namely, the height of the prewave is independent of the concentration of iodide when the latter is greater than $5 \times 10^{-5} M$ and is proportional to the height of the mercury column.¹⁰ The characteristics of adsorption waves are the same at the d.m.e. and at the r.d.m.e.¹¹

Electrocapillary Curves.—The presence of a small amount of iodide ions causes a large decrease in drop time (Fig. 3). Comparison of curve 2 in Fig. 3 with curve 3 in Fig. 2, both of which were obtained with $10^{-4} M$ iodide at the d.m.e., shows that the potential range where the depression occurs in the electrocapillary curve corresponds to that in which the anodic iodide wave is observed. In this potential range there should be no iodide ions present at the electrode surface since all iodide ions reaching the electrode surface precipitate quantitatively in the form of mercurous iodide because of its small solubility (the solubility product of Hg_2I_2 is equal to 4.5×10^{-29}).¹² Thus the observed depression of electrocapillary curve in the presence of a small amount of iodide must be attributed entirely to adsorbed mercurous iodide rather than to the adsorption of free iodide ions. The break in electrocapillary curve at about $+0.3$ v. appears to indicate that the film of mercurous iodide breaks

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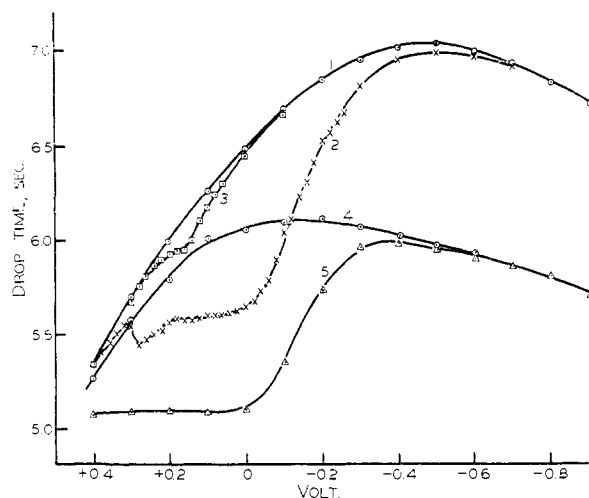


Fig. 3.—Electrocapillary curves (d.m.e. at $h = 44$ cm.): 1, $0.1 M HClO_4$; 2, $0.1 M HClO_4 + 10^{-4} M KI$; 3, $0.1 M HClO_4 + 10^{-4} M KBr$; 4, $0.1 M HClO_4 + 0.1\%$ Triton X-100; 5, composition of 4 + $10^{-4} M KI$.

down at this potential. Curve 3 in Fig. 3 gives indication of the formation of a film of mercurous bromide, but its effect on the electrocapillary curve is considerably smaller than that of iodide.

Curves 4 and 5 in Fig. 3 show that the addition of Triton X-100 considerably decreases the drop time both in the absence and presence of iodide. From a comparison of curves 1 and 4 in Fig. 3 it is clear that Triton X-100 in a concentration of 0.1% is strongly surface-active. The surface tension is more suppressed in the potential range where the iodide film is formed by addition of $10^{-4} M$ iodide (curve 5, Fig. 3). The results indicate that mercurous iodide and Triton are both adsorbed simultaneously and that no replacement of one film by the other takes place. Although Triton X-100 greatly distorts the anodic copper wave, current-potential curves of iodide are not affected by this surface-active substance.

Suppression of Maxima by Insoluble Films.—

Several examples are given in this section to demonstrate the strong suppressing effect of adsorbed insoluble films on maxima of both the first and the second kind. First of all, it should be mentioned that the current-potential curve of $1.5 \times 10^{-4} M$ iodide in $0.1 M$ perchloric acid at the r.d.m.e. ($h = 41.5$ cm.) in the presence of 0.01% polyacrylamide (PAA) was found to be practically the same as curve 5 in Fig. 2 which was recorded in the absence of PAA. This fact indicates that the anodic iodide wave at the r.d.m.e. does not involve maxima of the second kind which are observed at this electrode in the absence of a maximum suppressor.

An air-saturated solution of $0.02 M$ potassium nitrate exhibits an acute maximum of the first kind at the d.m.e. In Fig. 4 it is shown that this maximum is completely suppressed by iodide in a concentration as small as $10^{-5} M$. On the other hand, the oxygen wave in $0.02 M$ potassium iodide exhibits a maximum of the same nature and height as that in $0.02 M$ potassium nitrate, even though the iodide ion is strongly capillary-active. At this

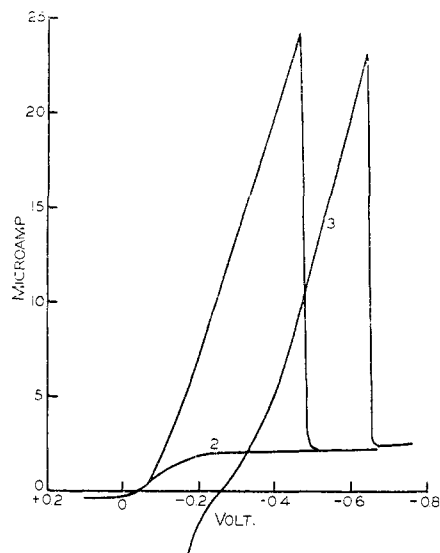


Fig. 4.—Effect of KI on oxygen maximum in air-saturated solutions at d.m.e. ($h = 51.5$ cm.): 1, $0.02 M KNO_3$; 2, $0.02 M KNO_3 + 10^{-5} M KI$; 3, $0.02 M KI$.

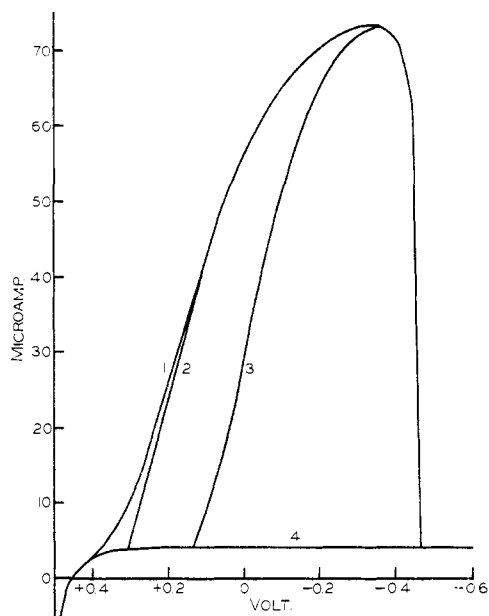


Fig. 5.—Effect of KCl, KBr and KI on ferric maximum in solution $2 \times 10^{-3} M$ in $Fe(NO_3)_3$ and $0.02 M$ in HNO_3 at d.m.e. ($h = 51.5$ cm.): 1, no halide; 2, $5 \times 10^{-5} M KCl$; 3, $10^{-5} M KBr$; 4, $10^{-5} M KI$.

large concentration of iodide apparently a soluble mercury-iodide complex is formed and no film of insoluble mercurous iodide is observed.

Effects of iodide, bromide and chloride on the pronounced maximum on the ferric wave in $0.02 M$ nitric acid are illustrated in Fig. 5. Again iodide eliminates the maximum entirely, while bromide and chloride were found to be effective only in a limited potential range, which apparently corresponds to the region where these ions give anodic waves. At the potential where no film is present the diffusion current suddenly increases to a large maximum of the same magnitude as in the absence of chloride or bromide.

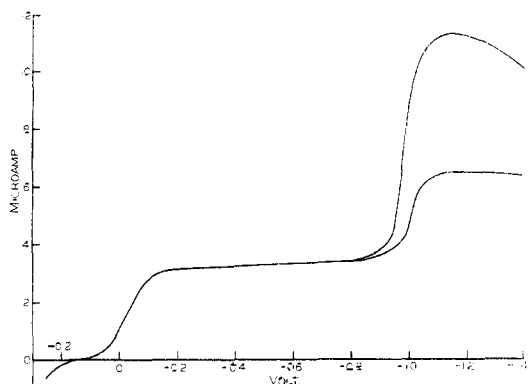


Fig. 6.—Reduction waves of $10^{-4} M$ $C_6H_5_2HgCl$ in $0.1 M$ acetate buffer (pH 4.6) at the r.d.m.e. ($h = 41.5$ cm.): 1, no PAA; 2, 0.01% PAA.

In addition to the examples illustrated above, we found that pronounced maxima of the first kind, appearing on polarograms of the following species, are completely eliminated by the addition of $10^{-5} M$ potassium iodide; mercury(II) and copper(II) in $0.1 M$ perchloric acid, persulfate in $0.1 M$ sodium perchlorate and lead in $0.02 M$ perchloric acid. Maxima of thallium in $0.1 M$ potassium chloride and of nickel in $0.1 M$ sodium perchlorate were not suppressed by the addition of $10^{-5} M$ iodide. No film of mercurous iodide is formed at potentials where these ions are reduced.

Phenylmercuric compounds are known to be subjected to a stepwise reduction at the d.m.e., the reduction product on the first wave being C_6H_5Hg which dimerizes to form insoluble diphenylmercury $(C_6H_5)_2Hg$ and mercury.^{3,4} In Fig. 6 are shown current-potential curves obtained at the r.d.m.e. with $10^{-4} M$ phenylmercuric chloride in $0.1 M$ acetate buffer at pH 4.6. It is seen that no maxima of the second kind occur on the first wave even in the absence of PAA, which supports the interpretation that insoluble diphenylmercury is formed and adsorbed on the mercury surface at potentials on the first wave. The reduction product formed on the second wave is benzene. It is evident from curves 1 and 2 in Fig. 6 that this reduction product does not suppress a maximum of the second kind. We also found that the addition of $10^{-5} M$ phenylmercuric chloride completely suppresses an acute maximum of the first kind observed at the d.m.e. with an air-saturated solution containing $0.02 M$ sodium acetate and $0.02 M$ acetic acid.

In connection with our study of the effect of various surface-active substances on polarographic waves, we found that the anodic copper wave at a dropping copper amalgam electrode possesses very peculiar characteristics in the absence of surface-active substances, although it has an appearance of a normal polarographic wave. The limiting current observed, for example, with $1.5 \times 10^{-3} M$ copper amalgam in $0.1 M$ perchloric acid in the absence of surface-active substances was found to be about 20% greater than that observed in the presence of substances such as PAA, Triton X-100, sodium dodecyl sulfate or dodecylamine perchlorate. Observation of amalgam drops

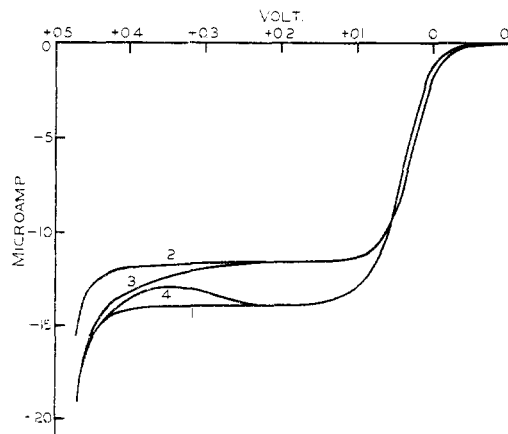


Fig. 7.—Effect of halide on the anodic copper wave in $0.1 M$ $HClO_4$. Concentration of copper amalgam: $ca. 1.5 \times 10^{-3} M$: 1, no halide; 2, $10^{-5} M$ KI; 3, $10^{-5} M$ KBr; 4, $10^{-5} M$ KCl.

with a microscope during the electrolysis of a solution containing a suspension of charcoal powder revealed that streaming occurred in the vicinity of the amalgam surface in the absence of surface-active substances. This streaming or "maximum" was observed even at a concentration of perchloric acid as small as $0.002 M$ at a drop time as great as 6 seconds. It was found that the limiting current decreases with increasing electrolyte concentration, which is a tendency exactly reverse to that observed when dealing with so-called maxima of the second kind. The peculiar "maximum" is completely suppressed by the above surface-active substances and, as is evident from Fig. 7, also by the addition of $10^{-5} M$ iodide or bromide, while chloride shows only a tendency to suppress it at potentials where mercurous chloride is formed anodically.

Variation of the Shape of Polarograms by Insoluble Films.—Effects of adsorbed surface-active anions on the mercury surface upon the rate of electrode reactions or the shape of polarograms have been discussed in recent literature by several investigators.¹³⁻¹⁹ When such surface-active anions depolarize the d.m.e. anodically and form a film of mercury salts, the characteristics of a current-potential curve may be affected in the potential range where the film is formed. A few such examples are given below.

Current-potential curves of copper(II) in $0.1 M$ perchloric acid in the absence and presence of trace amounts of iodide are shown in Fig. 8. No maxima occur at this small concentration of copper. The irreversible wave of copper is made more reversible by the addition of iodide, the effect being clearly observed at iodide concentration as small as $10^{-6} M$. This effect cannot be attributed to

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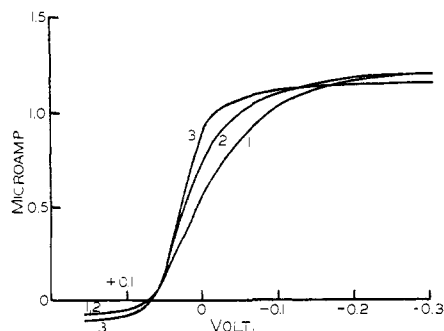


Fig. 8.—Effect of KI on the reduction wave of 2×10^{-4} M copper(II) in $0.1 M$ $HClO_4$ at d.m.e. ($h = 51.5$ cm.). Concentration of KI: 1, no KI; 2, $10^{-6} M$; 3, $10^{-5} M$. Not corrected for the residual.

the simple adsorption of iodide ions, because in the potential range where the copper wave appears free iodide ions reaching the electrode surface combine with mercury to form mercurous iodide (compare Fig. 8 with Fig. 1).

Distortion of the polarograms of persulfate in $0.1 M$ perchloric acid containing various amounts of iodide is illustrated in Fig. 9. It is seen in this

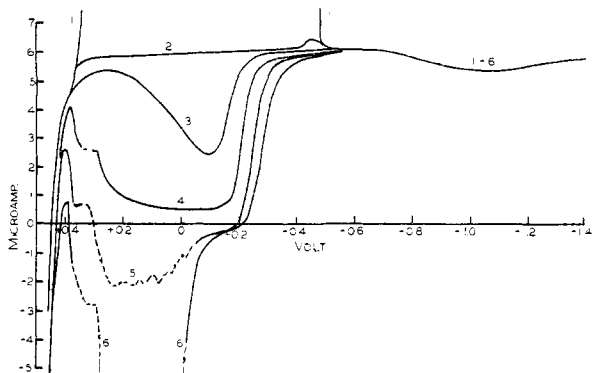


Fig. 9.—Effect of KI on the persulfate wave in solution $10^{-3} M$ in $K_2S_2O_8$ and $0.1 M$ in $NaClO_4$ at d.m.e. ($h = 44$ cm.). Concentration of KI: 1, no KI; 2, $10^{-6} M$; 3, $10^{-4} M$; 4, $2 \times 10^{-4} M$; 5, $5 \times 10^{-4} M$; 6, $10^{-3} M$.

figure that the depression of the diffusion current occurs only in the potential range where mercurous iodide is formed. With 10^{-4} to $2 \times 10^{-4} M$ bromide we observed a similar decrease of diffusion current of the persulfate wave at potentials more positive than $+0.1$ v. where mercurous bromide forms a film.

The first reduction wave of oxygen in $0.1 M$ sodium perchlorate, which appears also in the potential range where mercurous iodide film is formed, was found to be displaced by about 50 mv. to a more negative potential in the presence of $10^{-4} M$ iodide. Thus the film of mercurous iodide makes the oxygen wave more irreversible. A more interesting effect is exerted by phenylmercuric chloride. In Fig. 10 is illustrated the distorting effect of this substance on the oxygen wave in $0.1 M$ acetate buffer. It was confirmed that $10^{-4} M$ chloride ions do not affect the oxygen wave, and hence the observed effect of phenylmercuric chloride must be entirely due to either the phenylmercuric ion or its reduction product,

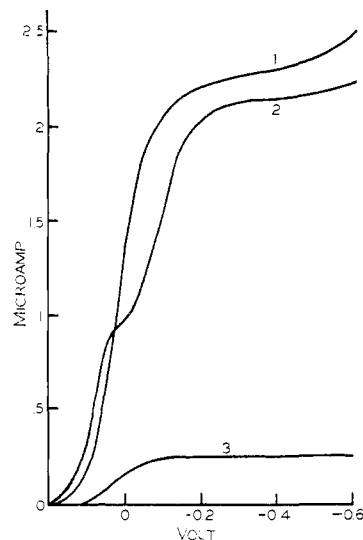


Fig. 10.—Effect of C_6H_5HgCl on the oxygen wave in solution $0.1 M$ in $NaAc$ and $0.1 M$ in HAc saturated with air at d.m.e. ($h = 44$ cm.): 1, no C_6H_5HgCl ; 2, $10^{-4} M$ C_6H_5HgCl ; 3, $10^{-4} M$ C_6H_5HgCl after deaeration. Currents corrected for the residual and for the current due to the reduction of C_6H_5HgCl .

diphenylmercury. It is noted in Fig. 10 that at potentials more positive than about $+0.05$ v. the current is greater in the presence than in the absence of phenylmercuric chloride. At these positive potentials practically no phenylmercuric chloride is reduced (see Fig. 6), and therefore a film of diphenylmercury must be absent at the electrode surface (compare curves 2 and 3 in Fig. 10). Presumably the increase in current at positive potentials arises from the adsorption of positively charged phenylmercuric ions, in accordance with Frumkin's theory of electrostatic effects on the rate of electrode reaction^{14,16} (see Discussion). The decrease in current at more negative potentials must be attributed to the insoluble film of diphenylmercury.

Discussion

Kolthoff and Miller³ found that the anodic chloride wave is reversible when the concentration of chloride is smaller than $1.5 \times 10^{-3} M$ and follows the theoretical equation

$$E = \text{const.} - 0.059 \log (i_d - i) \quad (1)$$

which is derived from the Nernst equation. Meites²⁰ states that this equation also holds for bromide and iodide ions. Anodic iodide waves both at the d.m.e. and at the r.d.m.e. shown in Figs. 1 and 2 were analyzed by plotting E vs. $\log (i_d - i)$. As shown in Fig. 11, part of the plots corresponding to potentials more negative than those where the surface of the mercury has been covered with a monomolecular layer are straight lines, the slopes of which were found equal to 104 and 98 mv. at the d.m.e. and at the r.d.m.e., respectively, as compared to the theoretical value of 59 mv. in equation 1 for a reversible reaction. These results clearly indicate that the main anodic iodide

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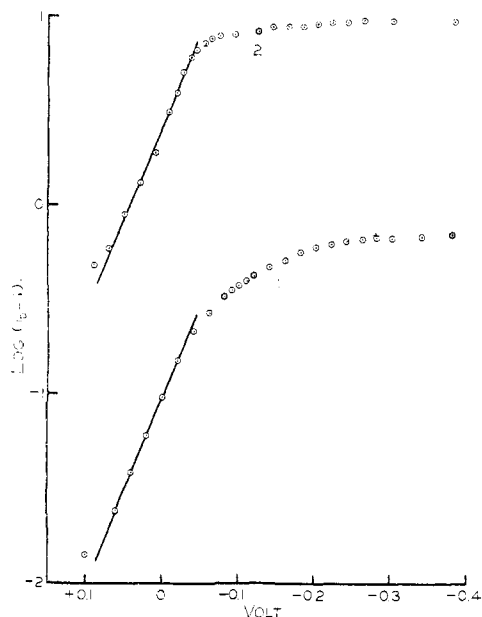


Fig. 11.—Analyses of anodic iodide waves at d.m.e. ($h = 44$ cm.) (curve 1) and at r.d.m.e. ($h = 41.5$ cm., 210 r.p.m.) (curve 2); 2×10^{-4} M KI in 0.1 M NaClO₄.

wave is irreversible, while the adsorption wave is still much more drawn out.

The anodic prewave of iodide is much more clearly visible at the r.d.m.e. (Fig. 2) than at the d.m.e. (Fig. 1). This must be attributed to the fact that the degree of irreversibility of a wave is greater at the r.d.m.e. than at the d.m.e.²¹ The main irreversible wave occurs at a more positive potential at the r.d.m.e. than at the d.m.e. at an identical concentration of iodide, while the adsorption wave appears at the same potential at both electrodes. It would seem that the irreversibility of the main iodide wave is caused by the inhibiting effect on the electron transfer by the adsorbed mercurous iodide film. For this reason it cannot be stated definitely that the appearance of the adsorption wave is brought about by the difference in activity between adsorbed and unadsorbed mercurous iodide.²²

From the above discussion and the results on maximum suppression described in the Experimental section, it is obvious that it is the film of mercurous iodide which is responsible for the suppression of maxima. Conclusive evidence is furnished by the fact that the oxygen maximum is suppressed with 10^{-5} M iodide but reappears at 0.02 M (Fig. 4). From the above interpretation of the iodide waves presented in Fig. 1 it may be concluded that at our dropping mercury electrode only an adsorption wave is found when the iodide concentration in the bulk of the solution is equal or smaller than about 10^{-4} M. This concentration is about ten times greater than that needed to suppress maxima completely at the d.m.e. In this respect the behavior of the film of mercurous iodide is similar to that of an organic maximum suppressor; the suppression of maxima is complete at a

much smaller concentration than required to form a monomolecular layer.

At the r.d.m.e. a complete monomolecular layer is formed at a smaller iodide concentration than at the d.m.e. because of the increased rate of transport of iodide ions to the electrode surface under the influence of convection. It is seen from Fig. 2 that formation of a monomolecular layer is complete at an iodide concentration of the order of 4×10^{-5} M at the r.d.m.e. under our experimental conditions. However, even at much smaller concentrations when the surface is covered with only a fraction of a monomolecular layer, complete suppression of a maximum of the second kind is found at the r.d.m.e.

As far as the effect of a mercurous iodide film on the characteristics of polarographic waves is concerned, it appears that the iodide film behaves like a negatively charged surface-active substance. The adsorption of a charged species changes the structure of the double layer, which affects the concentration of electroactive species near the electrode surface and the effective potential difference between the electrode and the point in the solution where the electrode reaction actually takes place.^{14,16} Frumkin's theory accounts for the variation of current resulting from the above two factors and predicts that the adsorption of a negatively charged substance accelerates the reduction of cations but decelerates the reduction of anions and uncharged species. The accelerating effect of dodecyl sulfate upon the reduction of aquo copper(II) ions at the d.m.e. has been accounted for¹⁸ on the basis of Frumkin's theory. Although it is not possible to present an exact picture of the structure of the double (or triple) layer in the presence of adsorbed mercurous iodide, it is fair to state that the iodide is oriented toward the aqueous layer and in this respect behaves like an anion of an organic surface-active substance. In agreement with Heyrovsky and Matyas²³ we observed that the copper wave is made more reversible also in the presence of small amounts of chloride ions. This effect must be attributed to the adsorption of copper(I) chloride formed during the reduction of Cu(II); a mercurous chloride film cannot be formed in the potential range where the copper wave appears.

Recently we reported that the copper(II) wave in perchloric acid solutions is split into two waves by the addition of Triton X-100.¹⁸ When the concentration of Triton X-100 is sufficiently large ($> 0.05\%$), the first wave becomes very small as compared to the second wave and controlled by the rate of penetration of aquo-copper ions through the adsorbed layer of Triton X-100. It was found that the height of the first wave is greatly increased when a small amount of iodide is added; and that this effect is extremely sensitive to trace amounts of iodide; for example, a concentration of iodide as small as 10^{-7} M could be clearly detected. We made a great number of experiments on the effect of a mixture of halide ions and various organic surface-active substances on the reduction of copper(II) and the oxidation of copper

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amalgam. As was anticipated, the results of these experiments are difficult to interpret, and details will be reported in a subsequent paper.

The effect of the *adsorption* of halide ions on the reduction wave of persulfate was studied by Kalish and Frumkin^{16,17} using much greater concentrations of halide (0.01 to 1 *M*) than used in our experiments. They found, for example, that the half-wave potential of the persulfate wave is about 0.6 v. more negative in 1 *M* potassium bromide than in 1 *N* sodium sulfate but made no mention of the effect of halide films such as we observed in the presence of small concentrations of iodide. From the results in Fig. 9 it is clear that 10⁻⁵ *M* iodide (curve 2) suppresses the extremely pronounced maximum (curve 1) observed in our supporting electrolyte. However, just at the potential (-0.4 v.) where the adsorption film disappears, a slight maximum still did occur. The waves observed in the presence of larger concentrations of iodide have a very abnormal appearance. Starting at the most positive potentials the current starts to rise and reaches a maximum which is considerably below the diffusion current. It appears that in this range the iodide does not affect the electrode process. The reason is clear from curve 2 in Fig. 3 which indicates that the film of mercurous iodide breaks down at potentials more positive than

+0.3 volt. Considering the persulfate wave in 10⁻⁴ *M* iodide (curve 3, Fig. 9), the monomolecular layer of mercurous iodide is being formed after the current attains a maximum value at about +0.4 v. This film interferes with the reduction of persulfate and the current decreases to a minimum value at -0.1 v. When the potential is being made more negative, the film is being dissolved and the current increases and attains the value of the diffusion current at -0.4 v. From the results at higher iodide concentrations (curves 5 and 6 in Fig. 9) it appears that multimolecular layers of mercurous iodide can entirely prevent the reduction of persulfate until potentials are attained where the film becomes less than monomolecular.

The first oxygen wave is made more irreversible by a film of mercurous iodide. Bagozkaya^{13,14} found that the adsorption of halide ions increases the overvoltage in the reduction of oxygen. Mancy and Okum¹⁹ also found that anionic organic surface-active substances make the oxygen wave more irreversible. Thus the effect of the adsorbed mercurous iodide film on the reduction of oxygen appears to be of the same nature as that of adsorbed anions.

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Cyanide Carbon Isotope Fractionation in the Reaction of Cyanide Ion and Methyl Iodide. Carbon Isotope Effect in the Hydrolysis of Methyl Iodide

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The C¹³ isotope effects for isotopy at the cyanide carbon in the cyanization of methyl iodide and that in the hydrolysis of methyl iodide have been investigated for water solvent over the temperature range 11.4 to 58°. The results for hydrolysis are somewhat smaller than expected from the single value reported by Bender and Hoeg for the C¹⁴ effect, being at the 3.5% level; the cyanide carbon isotope effect in the cyanization is only about 1.0%. The results are examined in terms of a Bigeleisen-Wolfsberg-Slater three-particle model for the reacting system, special attention being paid to the choice between "atomic" and "molecular fragment" masses in the calculation of the temperature-independent factor in the isotopic rate constant ratios. The data do not permit a clear choice to be made between these bases for the computations.

Introduction

The reaction of cyanide ions with an alkyl halide offers a particularly simple example of a carbon-carbon bond forming process. The kinetics of several such substitutions have been studied,¹⁻³ and their mechanisms are known to be S_N2 in character. The cyanizations of the methyl halides in particular seem to be sufficiently devoid of complexity to permit a reasonably straightforward comparison of experimental and theoretical carbon isotope effects.⁴ In this paper we report the results of experiments on the fractionation of C¹³ contained in cyanide ions during the cyanization of methyl iodide. Since methyl iodide is hydrolyzed very slowly under the conditions of the

reaction,⁵ data on the C¹³ fractionation in the hydrolysis and its temperature dependence were obtained also. (The C¹⁴ isotope effect in the methyl iodide hydrolysis in 50% aqueous dioxane, at 25° only, has been measured by Bender and Hoeg.⁶) The effect of this hydrolysis can be ignored in an ordinary kinetics study²; preliminary experiments on the methyl iodide cyanization in water solution⁷ indicated that the isotope fractionation in the cyanide carbon was small with respect to that occurring in the methyl carbon during hydrolysis, but correction for the latter effect need not be entertained though the results in the former case depend upon accurate knowledge of the isotopic constitution of

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