were displaced from their usual layer structure. Reduced interaction always caused enhanced polarization.

The dielectric properties of the polyamides show steep temperature coefficients; at 146°, 70° below its melting point, polyhexamethylene sebacamide has $\epsilon' \sim 48$, $\epsilon'' \sim 27$, at 1 kc. This compound also has a high frequency absorption as-

sociated with a relaxation process of activation energy 23.3 kcal. per mole, about twice the value for the analogous polyesters. Further, the polyamides show a high d. c. conductivity at elevated temperatures, which may be caused by mobile, charged atoms, such as hydrogen, resulting from isomerism in the amido linkage.

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The Dropping Mercury Electrode in Acetic Acid. II. Electrocapillary Curves and the Theory of Maxima[1,2]

BY G. BRYANT BACHMAN AND MELVIN J. ASTLE[3]

In a preceding paper[4] it was shown that ions and molecules with low polarographic reduction potentials give discontinuous current–voltage curves in acetic acid solutions. In the present investigation this phenomenon has been related to the adsorption processes occurring on the drop through a study of electrocapillary curves.

Discontinuities in anhydrous acetic acid are fundamentally the same phenomena as maxima in water systems. They differ in that they seem to be limited to substances of rather low reduction potential. Since the occurrences of maxima in aqueous solutions have been associated with the adsorption of ions and molecules on the mercury drop, it is reasonable to assume that a similar association exists in acetic acid solutions. A convenient method of studying adsorption on charged mercury surfaces is through the medium of electrocapillary curves.

The electrocapillary curve for ammonium acetate in anhydrous acetic acid shows a marked difference from the same curve in water in that the top of the curve is broad and rather flat and two maxima instead of one are present. Double maxima are very uncommon in water although Kemula and Beer[5] observed them in some cases using the dynamic drop weight method. Addition of water causes the two maxima in acetic acid to approach each other and to blend into one

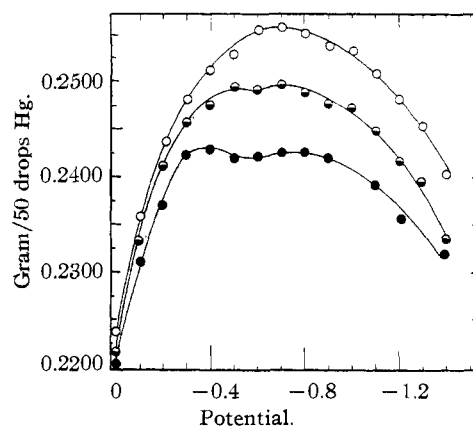well-defined maximum at 50 mole per cent. water (Fig. 1).

Fig. 1.—The effect of solvent composition on the electrocapillary curve for mercury in ammonium acetate solutions: ●, 0.25 M NH₄OAc in acetic acid; ◐, 0.25 M NH₄OAc in acetic acid and water (35 mole %); ○, 0.25 M NH₄OAc in acetic acid and water (50 mole %).

When salts are added to a solution of ammonium acetate in acetic acid, the effect on the electrocapillary curve depends on the reduction potential of the cation of the salt. If the cation has a half-wave reduction potential more negative than the *first* electrocapillary maximum for solutions of ammonium acetate in acetic acid (about −0.3 volt) then the resulting curves have the same general shape as the electrocapillary curve for ammonium acetate alone. Such cations are designated as Class I cations and include Zn^{++}, Pb^{++}, Cd^{++}, Co^{++}, Sb^{+++}, Ni^{++}, Cr^{+++} and Bi^{+++}. Figure 2 shows typical curves of this sort for Zn^{++} together with the corresponding current–

(1) Presented before the Physical and Inorganic Section at the Atlantic City meeting of the American Chemical Society, September 8–12, 1941.

(2) From the Ph.D. thesis of Melvin J. Astle.

(3) Present address: University of Kentucky, Lexington, Kentucky.

(4) Bachman and Astle, THIS JOURNAL, 64, 1303 (1942).

(5) W. Kemula and E. Beer, Roczniki Chem., 16, 259 (1936).

voltage curves. Solutions of these cations give normal S-shaped curves after degassing and can be determined polarographically in the usual fashion.
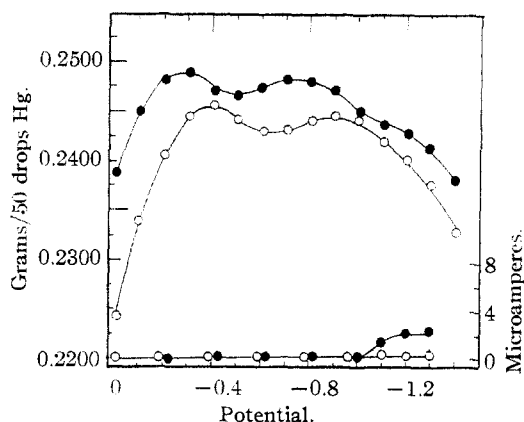

Fig. 2.—Electrocapillary curves (top) and current–potential curves (bottom): O, 0.25 M ammonium acetate; ●, 0.25 M ammonium acetate, 1.2 × 10⁻³ M zinc acetate.

Cations whose half-wave reduction potentials lie at more positive values than the first electrocapillary maximum for solutions of ammonium acetate in acetic acid give irregular and distorted electrocapillary curves. Such cations are designated as Class II cations and include Cu^{++}, Fe^{+++}, Pb^{++++} and Hg^{++}. The behavior of cations of this class is illustrated in Fig. 3 with electrocapillary and current–voltage curves for Cu^{++}. Class II cations cannot be determined polarographically in acetic acid even after their solutions are thoroughly degassed.
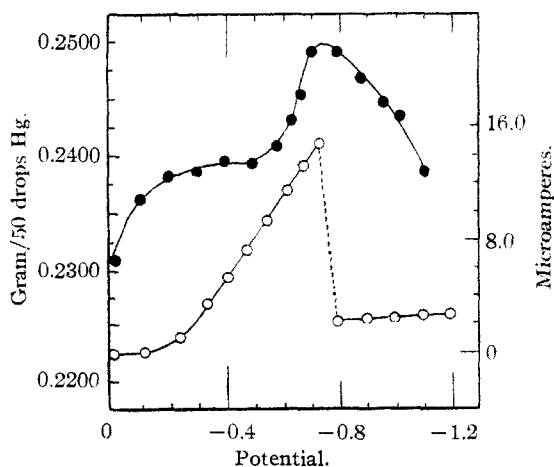

Fig. 3.—Electrocapillary and current–potential curves for the system ammonium acetate–copper acetate–acetic acid, 0.2 M ammonium acetate, 1.2 × 10⁻³ M copper acetate; ●, electrocapillary curve; O, current–potential curve.

An examination of Fig. 3 reveals that between −0.2 and −0.6 volt the surface tension remains practically constant.[6] In this region then there is no change in the degree of polarization and hence no change in the surface potential of the electrode. This is a result of the fact that the electrons flowing into the mercury drop from the external source are being neutralized by the reduction process. As the discontinuity potential is approached, however, the interfacial tension and the surface potential change very rapidly. Copper ions no longer reach the electrode in sufficient numbers to neutralize the flow of externally impressed electrons. Finally, the electrocapillary maximum is reached and passed, the mechanism of reduction changes radically as evidenced by the abrupt decrease in the current, and the electrocapillary curve becomes normal as the interfacial tension begins to parallel its decline in the absence of Cu^{++} ions.

Two important theories to account for maxima in current–voltage curves have been proposed. The first of these is that of Heyrovsky,[6] who attempted to explain them on the basis of the adsorption of the reducible substance on the growing drop. Ilkovic[7] also considers maxima as being caused by the adsorption of reducible substances on the mercury drop, but differs concerning the force responsible for it. The Heyrovsky and Ilkovic interpretations of maxima meet with much the same difficulties in attempting to explain the electrolysis of salts in acetic acid. In the first place, they do not take into account the change in sign of the drop charge at the maximum of the electrocapillary curve, and hence they do not explain the difference in the behavior of such ions as Cu^{++} and Zn^{++}. In the second place, it is difficult to understand, on the basis of this theory, the abrupt decline in the current which takes place in the reduction of Class II ions. Finally, it is probable that the thickness of the adsorption layer is insufficient to account for the manifold increase in adsorption required to produce the currents observed.[8]

A more recent theory of maxima has been put forward by Antweiler.[9] This theory is based on the observation that there is a vigorous stirring action around the mercury drop at potentials

(6) A similar phenomenon has been observed in aqueous solutions. Cf. Heyrovsky, "Actualités scientifiques et industrielles," No. 90, Hermann et Cie., Paris, 1934 .

(7) Ilkovic, Coll. Czech. Chem. Commun., 8, 13 (1936).

(8) Antweiler, Z. Elektrochem., 44, 831 (1938).

(9) Antweiler, ibid., 44, 663 (1938).

below that of the electrocapillary maximum, but that the stirring ceases and a well-defined diffusion layer forms at the potential of the maximum.[10] Streaming around the drop destroys the diffusion layer responsible for the concentration polarization and results in the carrying of many more ions to the drop than would otherwise reach it. The stirring action is electro-osmotic in nature and is caused by a tangential potential gradient which arises from a difference in current density between the top and bottom of the drop. The difference in current density is explained by Antweiler as being caused by a preferential adsorption of ions on the under side of the drop. The glass of the electrode partially shields the top of the drop and thus lengthens the path which the ions must travel in diffusing from the solution to the drop surface. Hence, the rate at which the ions are adsorbed is greater at the bottom than at the top of the drop.

The above reasoning accounts for the great increase in the current preceding the maximum but does not explain the sudden fall of the current beyond the maximum. To understand this it is necessary to consider the role of the supporting electrolyte. Taking as an example the electrolysis of Cu^{++} ions in the presence of Na^+ ions, it is clear that the Na^+ ions will wander to the cathode along with the Cu^{++} ions but that they will not be discharged, because of their higher reduction potential. The concentration of the Na^+ ions builds up, especially on the under side of the drop, with the result that the tangential potential is augmented still further and the streaming becomes still more rapid. This is accompanied by a rapid rise in the current. Eventually, however, the concentration of Na^+ ions becomes so high that the Cu^{++} ions are effectively screened out. When this occurs the current declines, the streaming ceases and normal concentration polarization sets in.

With certain additions and limitations this picture of current–voltage maxima can be carried over quite satisfactorily to reduction phenomena in acetic acid. In the electrolysis of Class II cations a maximum in the current–voltage curve is to be expected as a result of the streaming effect described above. The stirring brings to the drop an ever-increasing number of reducible cations. The current therefore rises more rapidly than would be expected on the basis of normal

(10) Antweiler, Z. Elektrochem., 44, 719 (1938).

diffusion. Two different processes now interrupt this rapid increase in the current. (1) The concentration of the supporting cations surrounding the drop may become so high that the ions being reduced are screened out. In this event reduction practically ceases, the current decreases, streaming stops, and a normal diffusion process of reduction is all that remains. (2) The maximum of the electrocapillary curve may be reached. If this occurs the charge on the drop surface becomes nil, and as a result the streaming ceases, the current drops abruptly, and once more a normal diffusion current is all that remains. It is evident that the second process is the one which applies to Class II cations. Our investigations indicate that the electrocapillary maximum always coincides with the potential of the discontinuity, even though the electrocapillary maximum may be shifted to more negative potentials as a result of the reduction process.

The addition of surface active substances would be expected to influence the nature of current–voltage curves to a considerable degree. All such substances are preferentially adsorbed on the mercury drop. They thus interfere with the adsorption of ions from the solution and prevent the establishment of a very high potential gradient. The result is that a more nearly normal diffusion process accompanied by less vigorous stirring is attained. Similar results would be expected with materials which raise the viscosity of the solution sufficiently to make streaming difficult. In Fig. 4 will be seen the effect of gelatin (saturated solution) on the reduction of copper in acetic acid. On the left there is a partially completed copper
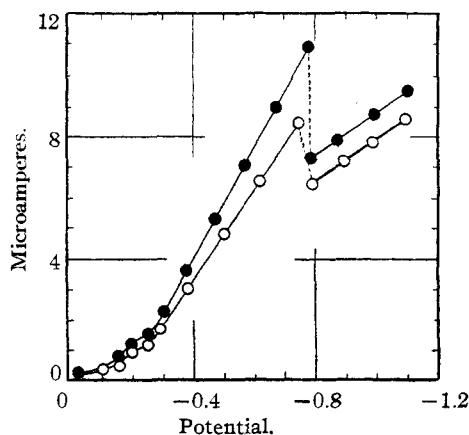
Fig. 4.—Current–potential curves in 0.25 molar sodium acetate solution in acetic acid containing gelatin: O, 10^{-1} molar copper acetate; ●, 2×10^{-1} molar copper acetate.

wave. This wave is almost normal, although the failure to level off at the top indicates that some streaming is occurring. Eventually the curve becomes discontinuous at the potential of the electrocapillary maximum.
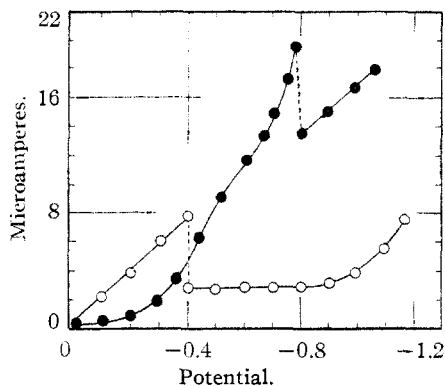

Fig. 5.—The effect of shifting the electrocapillary maximum on the current–potential curves in 0.25 molar ammonium acetate solutions in acetic acid: O, $1.14 \times 10^{-3}\ M$ benzil in presence of I^-; ●, $2 \times 10^{-4}\ M\ Bi^{+++}$ in the presence of NO_3^-.

On the negative side of the electrocapillary maximum the mercury drop is surrounded by adsorbed cations. The concentration of the adsorbed particles will again be greater at the bottom than at the top of the drop. *In water solutions* this results in a potential gradient and a streaming of the electrolyte. As before, a rapid rise in the current takes place as the reduction of the next ion begins. This is interrupted only when the concentration of the supporting ions becomes so great around the mercury drop that the ions being reduced are screened out. From this point on, the process follows the pattern previously discussed (Process 1 for ions of Class I). *In acetic acid* no maxima are observed on the negative side of the electrocapillary maximum. This arises from the fact that the electrocapillary curve in acetic acid is practically flat over the whole voltage range here studied. It was mentioned before that the adsorption of neutral molecules depresses and flattens electrocapillary curves. In this case neutral acetic acid molecules are probably adsorbed on the negative side of the maximum in sufficient concentration to prevent an appreciable adsorption of ions from the solution. Hence the established potential gradient is small, the stirring is negligible and maxima do not occur. The failure of surface active substances, which are often effective in reducing maxima in water solution, to function satisfactorily in acetic acid may be ex-

plained in the same way. These substances only tend to cause a broadening of the electrocapillary maximum such as is commonly observed in acetic acid without the addition of other substances. They, therefore, add nothing and detract nothing from the processes already occurring.

The addition of an ion which shifts the position of the electrocapillary maximum to more negative potentials causes the current–voltage curves for certain cations and other substances belonging to Class I to revert to Class II. Thus iodide ion causes the normal curves for bismuth ion and for benzil to become discontinuous (Fig. 5). These substances have half-wave reduction potentials which lie just beyond the electrocapillary maximum on the negative side. In the case of bismuth ions even nitrate ions, which are less powerful than iodide ions in shifting the maximum, can cause a discontinuity to appear.

In aqueous solutions most maxima are rounded in appearance although discontinuous maxima are also observed, especially in solutions of low ionic concentration. Usually discontinuous maxima can be made continuous by the addition of strongly adsorbed substances or by increasing the ionic concentration. Rayman[11] obtained discontinuous maxima for oxygen in 0.001 N potassium chloride solution. These became rounded humps when various dyes were added. Similarly, Dillinger[12] added barium chloride to make the discontinuous maxima of dilute mercurous cyanide solutions continuous. The discontinuous maxima in acetic acid are probably a result of the high resistances brought about by the low ionic concentrations possible in a medium of such low dielectric constant. The addition of water permits greater ionization and lower resistance and results in the occurrence of normal rounded maxima. The greater the concentration of the supporting ion, the less water is needed to effect this transformation.

The removal of all traces of oxygen is a *sine qua non* for the obtaining of satisfactory current–voltage curves in acetic acid. Even with relatively concentrated solutions of zinc salts the zinc wave is so small that it is completely obscured by the oxygen normally dissolved in the solution. Since there is ordinarily no discontinuity in the oxygen curve it is evident that it is reduced at potentials more negative than the electrocapillary maximum

(11) B. Rayman, *Coll. Czech. Chem. Commun.*, **3**, 314 (1931).
(12) Dillinger, *ibid.*, **1**, 638 (1929).

and hence belongs to the substances of Class I. However, it is thrown into Class II by the addition of small amounts of iodide ion (Fig. 6). Its reduction potential in acetic acid is therefore not far from that of bismuth ions.

Conclusions

1. The relationship which exists between the electrocapillary maximum of the medium and the half-wave potential of a reducible substance determines to a considerable degree the nature of the current–voltage curves of the substance in acetic acid and probably also in other solvents.

2. Class I substances, which are reduced at potentials more negative than the electrocapillary maximum, exhibit normal electrocapillary curves. They also give normal S-shaped current-voltage curves (after thorough degassing) and can be determined polarographically in the usual fashion. Class II substances, which are reduced at potentials more positive than the electrocapillary maximum, exhibit distorted electrocapillary curves. They also give discontinuous maxima in their current–voltage curves and cannot be determined polarographically.

3. Maxima in acetic acid can be explained satisfactorily on the basis of a streaming of the electrolyte around the mercury drop of the type observed by Antweiler for aqueous solutions. The decline in current following the maximum is caused by a screening out of the reducible ions by the supporting ions, or by the neutralization of charge on the drop occurring at the electrocapillary maximum, whichever occurs first.

4. Ions (like iodide) which shift the position of the electrocapillary maximum to more negative potentials cause certain reducible substances (like oxygen, bismuth ion and benzil) to change from Class I to Class II. Such substances have half-wave reduction potentials close to and on the negative side of the electrocapillary maximum.

5. Things which act to decrease the amount of adsorption of ions on the drop or the amount of streaming around the drop decrease the heights of the maxima. The addition of high molecular weight substances (like gelatin) which increase the viscosity, and the addition of capillary active substances (like methyl red) which decrease the adsorption of small ions by being adsorbed themselves both tend to decrease maxima heights. None of these substances is as effective in acetic acid solutions as in water because acetic
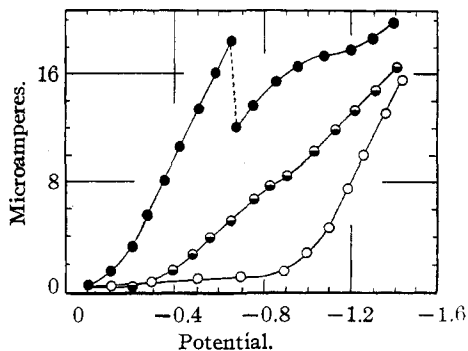

Fig. 6.—Current–potential curves for oxygen in acetic acid solutions: ◐, 0.25 molar ammonium acetate; ●, 0.25 molar ammonium acetate to which a small crystal of KI was added; ○, the latter solution after degassing for one hour.

acid molecules are themselves adsorbed fairly strongly.

Apparatus and Materials

The electrocapillary curves were determined by the drop weight method.[13] An electrolysis cell constructed in such a way as to make it possible to catch the drops falling from the dropping mercury cathode was attached to a Fisher Elecdropode identical with the one employed in our previous work. The dropping electrode was also identical with the one previously described. The capillary used had a value for $m^{2/3}t^{1/6}$ of 1.1 mg.$^{2/3}$ sec.$^{-1/2}$. After thoroughly degassing the solution to be studied, 50 drops of mercury were collected at each of a number of successively increased potentials. The mercury was then washed, dried and weighed. Since the surface tension is directly proportional to the drop weight, it is only necessary to plot this latter quantity against the potential to obtain curves which are strictly analogous to true electrocapillary curves and which do not differ from them in any detail of form or shape. The potentials plotted were corrected for the IR drop of the solutions. This correction is large in the case of acetic acid solutions.

The acetic acid was the "99.5%" acid of the J. T. Baker Chemical Company and was employed without further purification. The salts were all c. p. grade and were carefully dried at 110° before use. The organic materials were Eastman Kodak Co. grade, and were recrystallized once before use. Degassing was accomplished as before with purified natural gas.

Summary

A study of the electrocapillary curves of mercury in acetic acid solutions of various salts reveals some important differences from similar curves in aqueous solutions. With the aid of such curves it has been possible to explain the current–potential curves of various cations and other reducible substances in acetic acid.

(13) Heyrovsky and Dillinger, Coll. Czech. Chem. Commun., 2, 626 (1930).