[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Some Polarographic Effects of Gelatin and Other Maximum Suppressors

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The recent literature has contained a number of reports that such materials as methyl red and gelatin can radically alter the characteristics of a polarographic wave.[1-8] The present paper is a continuation of some earlier preliminary work on the effects of gelatin.[7]

Experimental

The polarographic apparatus will be described elsewhere. All measurements were made at 25.00 ± 0.05°. Dodecyl- and hexadecyltrimethylammonium bromides were prepared from trimethylamine and the corresponding alkyl bromide. Sodium laurate and myristate were kindly furnished by the Research Department of the Colgate-Palmolive Peet Co. "Bacto" gelatin (Difco Laboratories, Inc., Detroit), made by acid hydrolysis and clarification,[9] was swelled in water at 25° for one hour, then dissolved by warming briefly to 60° and diluted to volume. Triton X-100, a polyethylene glycol ether of monoisoöctylphenol, was considered to contain 100% active material as received from the Rohm and Haas Co. "Bacto" agar (Difco Laboratories, Inc.) was dissolved by boiling briefly with water and cooling rapidly. Methyl red (General Chemical Co., New York City) was dissolved in very dilute sodium hydroxide and neutralized to *p*H 9 with sulfuric acid. Gum arabic, U. S. P. XIII (Mallinckrodt Chemical Works), was dissolved in warm water.

All *p*H measurements are referred to a saturated solution of recrystallized potassium hydrogen tartrate, whose *p*H was taken as 3.57.[10]

Results

The effect of gelatin on the electrocapillary curve[11,12] in a typical case is shown in Fig. 1. No effect is observed with 0.001% gelatin, but 0.01% gelatin decreases the drop time over the entire range of potentials by about 5%, and 0.1% gelatin causes a further 5% decrease. Since this effect differs from those of most other capillary-active substances in that the latter are substantially without effect on the electrocapillary curve at very negative potentials, we instituted a systematic study of the effect of gelatin on the drop time at −0.5 v., which was near the electrocapillary maximum in all the solutions studied. In no case was there a maximum in any c.-v. curve at or near −0.5 v.; such a maximum would, of course, have invalidated the data.

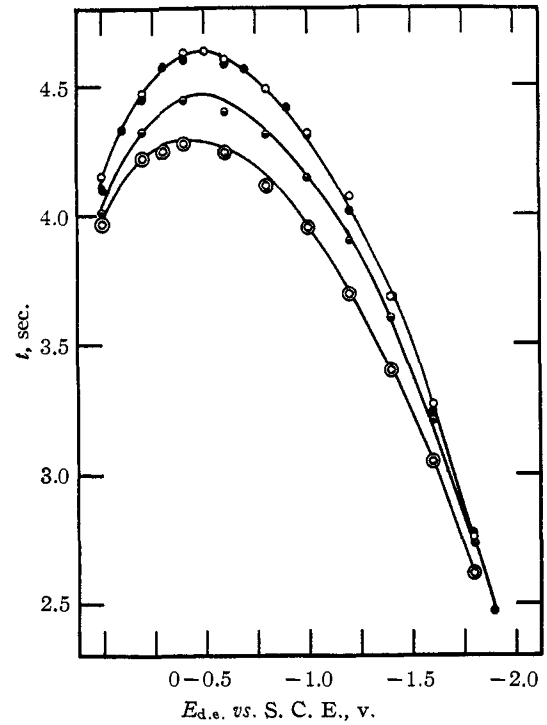

Fig. 1.—Electrocapillary curves in 0.10 *F* potassium chloride containing (a) 0 (open circles), (b) 9.80×10^{-4} (solid circles), (c) 1.06×10^{-2} (half-solid circles), and (d) 1.20×10^{-1} (double circles) % gelatin.

Although they show the relation between interfacial tension and drop time to be a complicated one, the Harkins–Brown equation[13] and the fact that *m* is nearly independent of the interfacial tension[14] show that *t* is a function of 0 alone with any given driving pressure and any one capillary. Therefore a discontinuity in the interfacial tension-concentration curve for a surface-active material can be located by finding the point at which a discontinuity occurs in the drop time-concentration curve.

Figure 2 shows several typical curves for gelatin in various media. Each point was secured by timing several sets of five or ten drops, and the individual values generally agreed to within 0.005 second.

The measurements with methyl red must be made at potentials between +0.15 v. and −0.3 v., where the dye is neither oxidized nor reduced. (The reduction at the dropping electrode is well known,[15] but the oxidation, for which the half-wave potential is +0.206 ± 0.002 v. in 0.1 *F* phosphate, *p*H 7.0, seems not to have been reported.) At potentials outside this range, the methyl red is destroyed as it reaches the drop surface, and no discontinuity is observed in the drop time-concentration curve (Fig. 3 I).

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(1) K. Wiesner, *Coll. Czechoslov. Chem. Communs.*, **12**, 594 (1947).

(2) R. H. Coe and L. B. Rogers, THIS JOURNAL, **70**, 3276 (1948).

(3) H. A. Laitinen, J. C. Bailar, Jr., H. F. Holtzclaw, Jr., and J. V. Quagliano, *ibid.*, **70**, 2999 (1948).

(4) C. A. Reynolds and L. B. Rogers, *Anal. Chem.*, **21**, 176 (1949).

(5) C. A. Reynolds, *ibid.*, **21**, 759 (1949).

(6) J. J. Lingane, THIS JOURNAL, **65**, 866 (1943).

(7) L. Meites, *ibid.*, **71**, 3269 (1949).

(8) F. Buckley and J. K. Taylor, *J. Research Natl. Bur. Standards*, **34**, 97 (1945).

(9) H. W. Schoenlein (Director, Difco Laboratories, Inc.), private communication.

(10) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **19**, 810 (1947).

(11) A. Frumkin, *Ergeb. exakt. Naturw.*, **7**, 235 (1928).

(12) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 96–104.

(13) W. D. Harkins and F. E. Brown, THIS JOURNAL, **41**, 499 (1919).

(14) Ref. 12, p. 64.

(15) Ref. 12, p. 120.

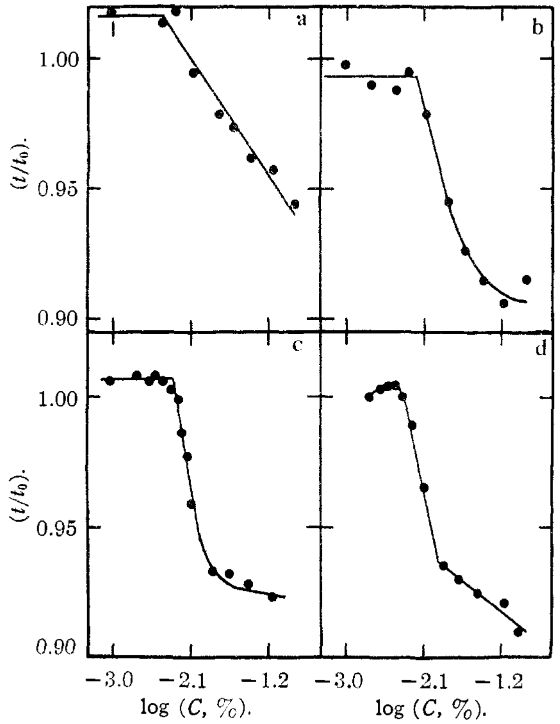

Fig. 2.—Effect of gelatin concentration on drop time at $E_{d.e.}$ = −0.5 v. in solutions containing (a) 4 m*M* nickel (II) in *F* potassium thiocyanate, (b) 3.5 m*M* vanadium (IV) in *F* potassium oxalate, pH 5.5, (c) 1 m*M* cyanide in 0.1 *F* potassium hydroxide, and (d) 4 m*M* bismuth (III) in 0.7 *F* perchloric acid.

Paralleling the discontinuity in the interfacial tension–concentration curve, we have found a sharp decrease in the diffusion coefficient of methyl red occurring at the same concentration. Figure 3 II shows the anodic diffusion current of methyl red in 0.1 *F* phosphate, *p*H 7.0, as a function of concentration. At concentrations above 6.5 × 10^{-4}% the slope of the line (according to the Ilkovič equation $\Delta i_d/\Delta C = kD^{1/2}$, neglecting the relatively small variation in $t^{1/6}$) drops suddenly to about one-tenth its value in more dilute solutions, corresponding to about a hundred-fold decrease in the diffusion coefficient.

These phenomena are strikingly analogous to the reported discontinuities in surface[16,17] and interfacial[16,18] tensions and diffusion coefficients[19] of materials which form micellar aggregates in solution. It would, indeed, appear difficult to avoid the conclusion that the discontinuities located by the above methods actually correspond to the classical "critical concentration for micelle formation." As will be shown, these same discontinuities correspond within the limits of experimental error to discontinuities in the variation of either the half-wave potential or diffusion current constant (or both) with the concentration of surface-active material. While we have no doubt that all of these methods serve to locate the "critical concentration for micelle formation," we shall, for the present, denote the concentration thus found by the term "polarographic critical concentration."

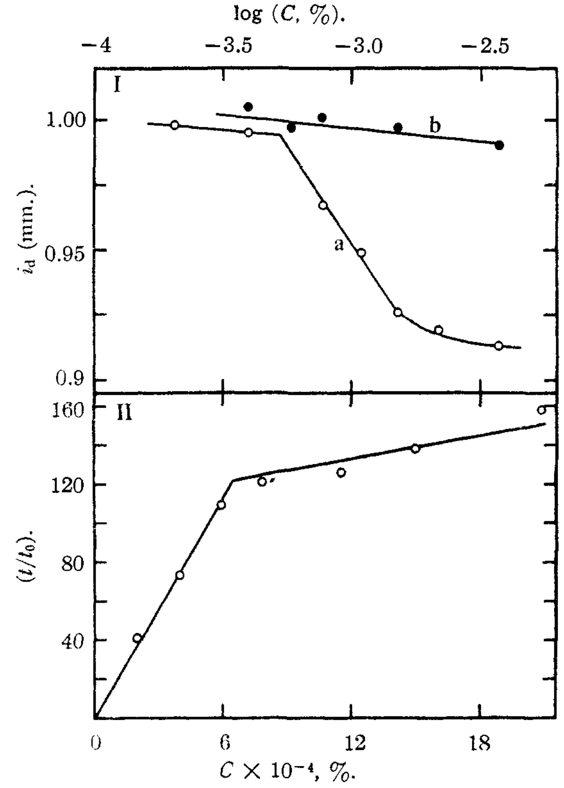

Fig. 3.—(I) Effect of methyl red concentration on drop time in 0.1 *F* phosphate, *p*H 7.0, at $E_{d.e.}$ = (a) −0.30 v., and (b) −0.40 v. (II). The anodic diffusion current of methyl red in the same medium, measured at $E_{d.e.}$ = +0.26 v.

However, since the formation of micellar aggregates in aqueous gelatin solutions seems not to have been conclusively established[20,21] and since gum solutions have not been studied at all from this viewpoint, we have measured the turbidities of typical solutions we have used, by light-scattering methods. These measurements were made with a B-S Light Scattering Photometer (Phoenix Precision Instrument Co., Philadelphia), using the blue 4370 Å. filter supplied with the instrument, and represent 90° scattering. From the results shown in Fig. 4a, the critical concentration for micelle formation of gelatin in 0.1 *F* potassium hydroxide lies between 3 and 4.5 × 10^{-3}%: the polarographic critical concentration from drop time data is 4.0 × 10^{-3}%. Figure 4b shows that the critical concentration for gum arabic in water is between 2 and 3 × 10^{-3}%.

The purely polarographic phenomena may be divided into six general classes, depending on the effects of the surface-active material at concentrations above the polarographic critical concentration. The specific causes of these effects are as yet impossible to determine. An ion which

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(16) J. Powney and C. C. Addison, *Trans. Faraday Soc.*, **33**, 1243 (1937).

(17) H. V. Tartar, V. Sivertz and R. E. Reitmeier, THIS JOURNAL, **62**, 2375 (1940).

(18) J. Stauff, *Z. physik. Chem.*, **A191**, 69 (1942).

(19) O. Lamm, *Kolloid-Z.*, **98**, 45 (1942).

(20) J. Loeb, in "The Theory and Application of Colloidal Behavior," R. H. Bogue, ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1924, Vol. I, pp. 35–39.

(21) J. W. McBain, *ibid.*, pp. 418–419.

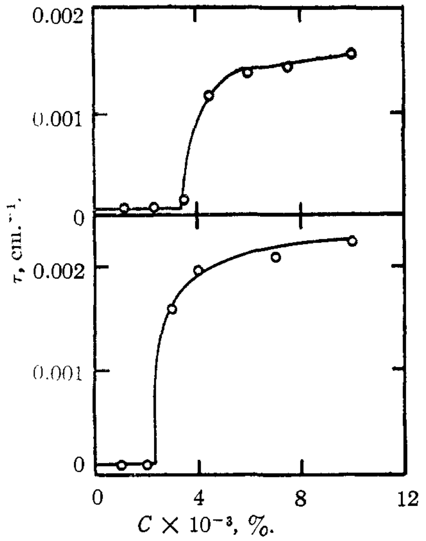

Fig. 4.—Turbidities of solutions of (a) gelatin in 0.10 F potassium hydroxide, and (b) gum arabic in water.

falls into one class with one surface-active material may show an entirely different sort of behavior with another, and two chemically very similar ions may behave quite differently.

From the many systems we have studied,[22] we have selected a few as typical of these classes for more detailed discussion.

I. *No Effect on Either* $E_{1/2}$ *or* $I\ (= i_d/Cm^{2/3}\cdot t)^{1/6}$.[23] Only about 10% of these nearly seventy systems belong to this class. Perhaps, significantly, more ions show this type of behavior with methyl red than with either gelatin or Triton X-100. Benzohydroquinone is the only substance which falls into this class with all three of these surface-active agents.

II. $E_{1/2}$ *is Unaffected, but* I *is* (*a*) *Increased or* (*b*) *Decreased.* This class is apparently the rarest of all. In subclass (a) we have found only thallium(I) in neutral F potassium nitrate with methyl red, and the entire increase in the diffusion current constant from 0 to 0.01% methyl red is only about 5%.

Subclass (*b*) is typified by zinc in F potassium chloride with methyl red (Fig. 5a). The diffusion current constant is unaffected by concentrations of the dye below 1.1×10^{-3}%, but higher concentrations cause a continuous decrease. As there is no accompanying change in the shape of the wave, which at all methyl red concentrations satisfies the criterion for "diffusion control" advanced by Buckley and Taylor,[8] it seems difficult to explain this result as a form of maximum suppression.

III. I *is Unaffected, but* $E_{1/2}$ *Becomes* (*a*) *More Positive or* (*b*) *More Negative.*—Positive shifts of the half-wave potential, in our experience, are generally rather small. Thus, $E_{1/2}$ of thallium(I) in F potassium nitrate is -0.472 ± 0.002 v. without gelatin and -0.453 v. (independent of gelatin concentration) at gelatin concentrations higher than about 6×10^{-2}%. The half-wave potential of cyanide ion in 0.1 F potassium hydroxide is -0.360 ± 0.005 v. without a maximum suppressor, and -0.333 v. with 0.04% or more Triton X-100. The discontinuities in plots of data on such systems as these are, of course, difficult to locate accurately, but there is certainly no doubt that they represent real effects (*cf.* Fig. 5b).

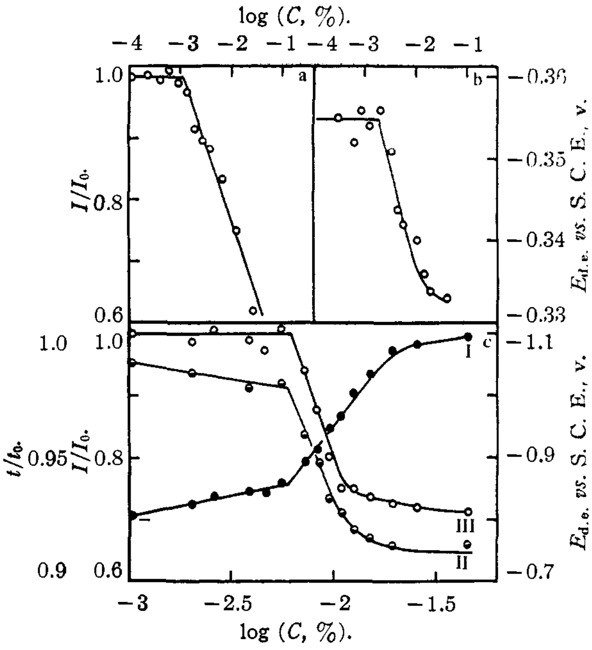

Fig. 5.—(a) Effect of methyl red on the diffusion current constant of zinc (II) in F potassium chloride; (b) effect of Triton X-100 on the half-wave potential of cyanide in 0.1 F potassium hydroxide; (c) effects of gelatin on the half-wave potential (curve I) and diffusion current constant (curve II) of the first iron (III) wave in F potassium fluoride, and on the drop time (curve III) in the same medium at -0.5 v.

Shifts to more negative potentials, however, are less predictable in magnitude. At one extreme, Triton X-100 alters $E_{1/2}$ of thallium(I) in F potassium nitrate from -0.472 v. only to -0.483 ± 0.002 v. At the other, gelatin at concentrations above about 8×10^{-3}% shifts $E_{1/2}$ of nickel(II) in 5 F ammonia–0.1 F ammonium chloride abruptly from -1.140 v.[24] to -1.176 v., and Triton X-100, at concentrations higher than 10^{-2}%, gives $E_{1/2} = -1.300 \pm 0.005$ v.

IV. I *Decreases and* $E_{1/2}$ *Becomes More Negative.*—This, of course, is merely a combination of classes IIb and IIIb, and, while three other combinations of effects are theoretically possible, we have found no examples of them. Figure 6 illustrates the phenomena observed in a typical case: data measured from this figure give the polarographic critical concentration as 4.9 ×

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(22) A table summarizing the authors' data on the polarographic critical concentrations of the substances studied, and their effects on the half-wave potentials and diffusion current constants of a variety of reducible materials, is available as Document No. 2833 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $0.50 for photocopies (6 × 8 inches) readable without optical aid.

(23) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

(24) This is the value measured with 0.008% gelatin: the large maximum with lower concentrations renders the apparent half-wave potentials meaningless.

$10^{-3}\%$ based on the discontinuity in $E_{1/2}$, or as $5.9 \times 10^{-3}\%$ from diffusion current measurements. The difference corresponds to an error of about 0.03 unit in the logarithm of each concentration. (The logarithm of the concentration of surface-active material is used in the analysis of the data simply because, as noted by Coe and Rogers,[2] it allows the data to be reproduced by straight lines over a considerable concentration range.)

Another typical example is the reduction of iron(III) from *F* potassium fluoride, *p*H 7.1, with gelatin (Fig. 7). Stackelberg and Freyhold[25] reported that this reduction proceeded only to the +2 state at $E_{1/2}$ = 1.40 v., but there are actually two waves: one, at $E_{1/2} = -0.94 \pm 0.01$ v., representing reduction to iron(II), and the other, twice the height of the first, at $E_{1/2} = -1.44 \pm 0.01$ v., corresponding to further reduction to the metal. The data on the first of these waves are plotted in Fig. 5c together with the drop-time data for comparison: the discontinuities in all three curves occur at 6.0 ($\pm$0.1) $\times 10^{-3}\%$ gelatin.

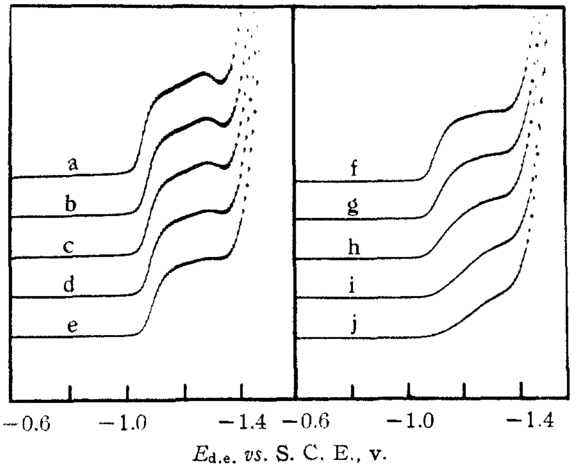

Fig. 6.—Polarograms of 4 m*M* cobalt (II) in 0.1 *F* pyridine–0.1 *F* pyridinium chloride with (a) 0, (b) 0.945, (c) 1.85, (d) 3.70, (e) 5.94, (f) 8.08, (g) 13.2, (h) 20.6, (i) 34.8, and (j) 66.9 $\times 10^{-3}$ % gelatin.

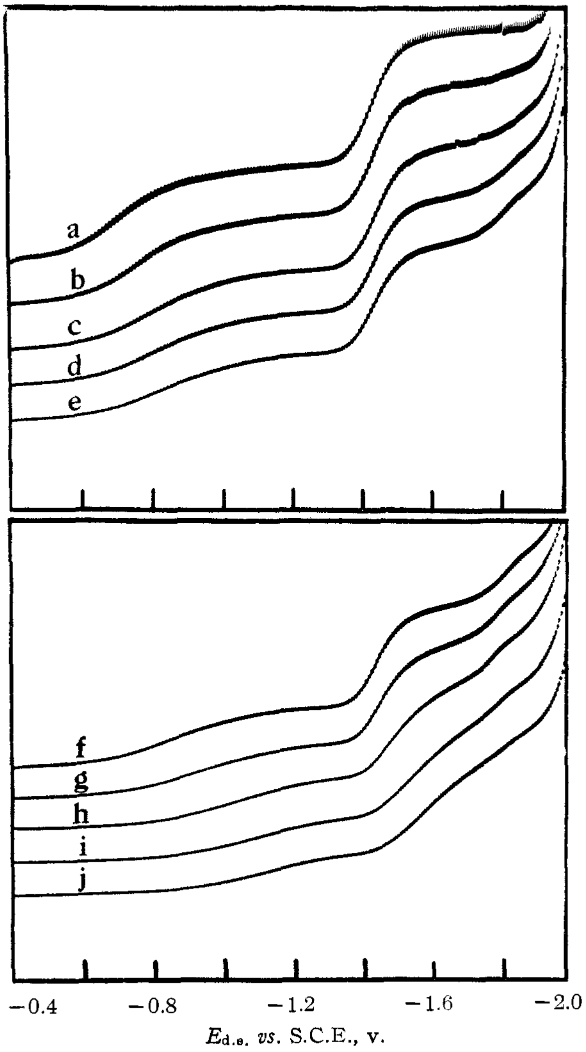

Fig. 7.—Polarograms of *F* potassium fluoride, *p*H 7.1, saturated with K_3FeF_6 (*ca.* 0.9 m*M*), with (a) 0, (b) 0.965, (c) 2.03, (d) 3.90, (e) 6.16, (f) 8.24, (g) 15.2, (h) 25.8, (i) 45.8, and (j) 89.0 $\times 10^{-3}$ % gelatin.

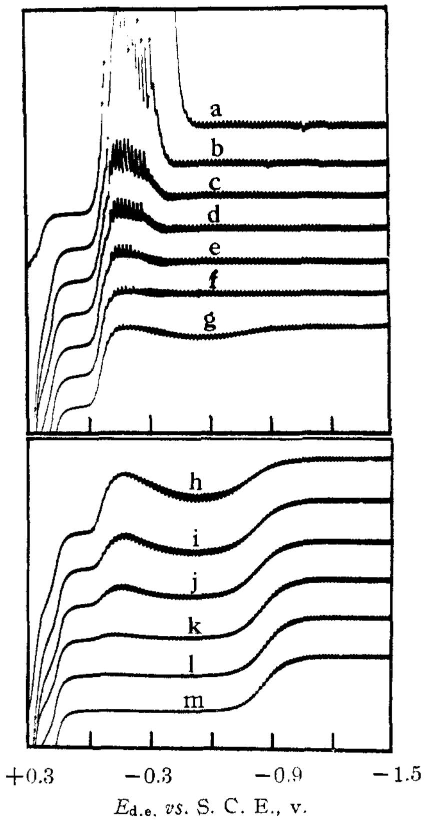

Fig. 8.—Polarograms of 4 m*M* copper (II) in *ca.* 0.09 *F* (saturated) potassium sodium tartrate, *p*H 4.00, with (a) 0, (b) 3.00, (c) 5.95, (d) 8.84, (e) 11.6, (f) 17.2, (g) 22.4, (h) 32.6, (i) 47.2, (j) 63.7, (k) 111, (l) 248, and (m) 448 $\times 10^{-4}$ % Triton X-100.

V. *A Wave is Broken into Two Parts, Always by the Formation of a New Wave at a More Negative Potential. Increasing the Concentration of Surface-active Material Increases the Height of the*

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(25) M. v. Stackelberg and H. v. Freyhold, *Z. Elektrochem.*, **46**, 120 (1939).

New Wave at the Expense of the Original One.—A good example is the effect of Triton X-100 on the reduction of copper(II) from an acidic tartrate supporting electrolyte (Fig. 8). It may be possible to take advantage of this type of behavior to separate two overlapping waves by the addition of a high concentration of some maximum suppressor.

A more complex example is found in the reduction of nickel(II) from *F* potassium thiocyanate in the presence of Triton X-100 (Fig. 9), where the original wave at $E_{1/2} = -0.678 \pm 0.003$ v. is replaced by another at about -1.6 v. At very high concentrations of Triton the new wave shifts to a somewhat more positive potential, and its height increases so that it is actually larger than that of the original wave. As shown by Fig. 10a, the original wave is divided into two parts (curve 1) even below the polarographic critical concentration, but the division is very greatly accentuated by Triton at an only slightly greater concentration. This sort of plot (curve 2) is characteristic of waves with rounded tops such as curve e, Fig. 9.

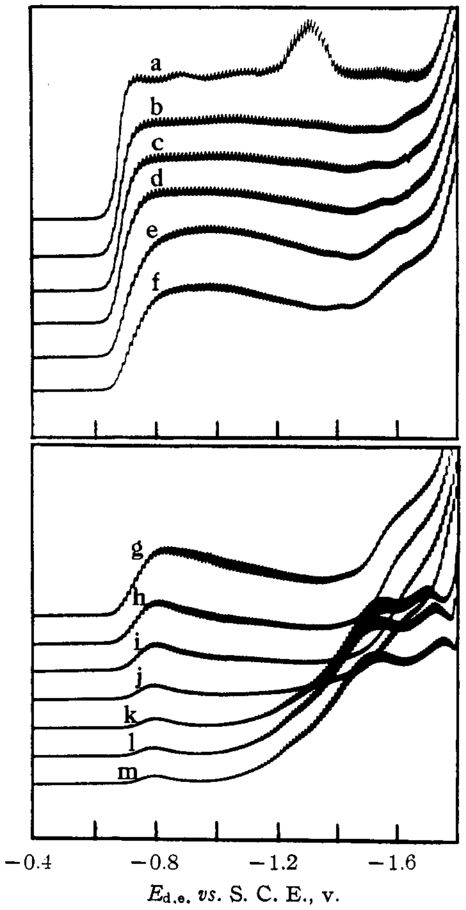

Fig. 9.—Polarograms of 4 mM nickel (II) in *F* potassium thiocyanate with (a) 0, (b) 2.94, (c) 5.83, (d) 8.65, (e) 14.2, (f) 19.5, (g) 29.6, (h) 43.5, (i) 60.0, (j) 106, (k) 195, (l) 318, and (m) 502×10^{-4} % Triton X-100.

VI. *An Originally Irreversible Wave is Shifted to More Negative Potentials and Becomes More Nearly Reversible.*—This type of behavior is demonstrated by copper(II) in a strongly alkaline tartrate solution. Figure 11 shows the effect of gelatin on this polarogram. The first wave (*cf.* curve a) is due to the two-electron reduction of a complex which may stoichiometrically be formu-

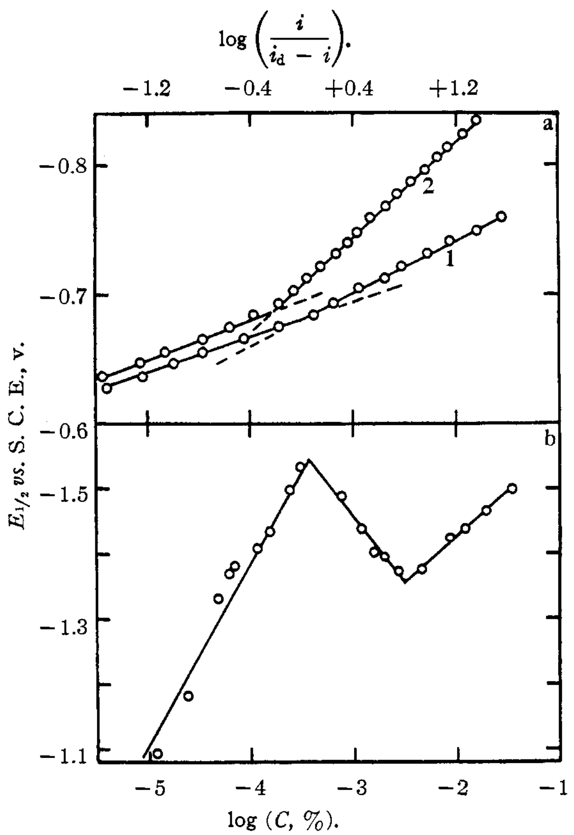

Fig. 10.—(a) Plots of $E_{d.e.}$ vs. *log* $(i/(i_d - i))$ for nickel (II) in *F* potassium thiocyanate with (1) 5.83 and (2) 14.2×10^{-4} % Triton X-100; (b) effect of dodecyltrimethylammonium bromide on the half-wave potential of the "second" wave of copper (II) in 0.5 *F* potassium sodium tartrate and *F* potassium hydroxide.

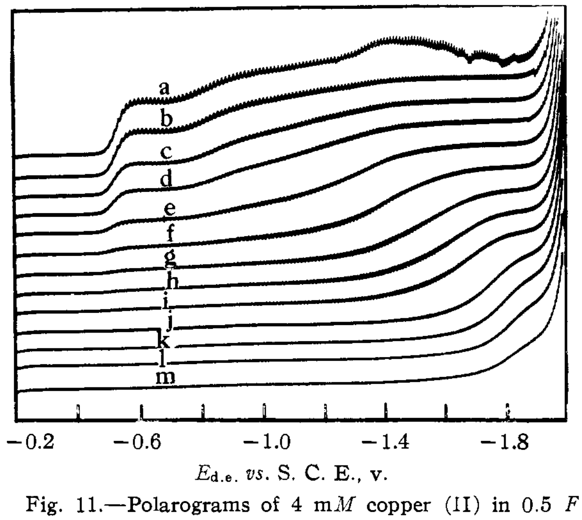

Fig. 11.—Polarograms of 4 mM copper (II) in 0.5 *F* potassium sodium tartrate–*F* potassium hydroxide with (a) 0, (b) 1.02, (c) 2.00, (d) 2.94, (e) 4.72, (f) 6.40, (g) 7.97, (h) 9.42, (i) 10.8, (j) 18.8, (k) 34.0, (l) 55.4, and (m) 87.1×10^{-3} % gelatin.

lated as $Cu(OH)_2(Tart)_2^{-4}$, and the "second" very long complex wave is due to the reduction of several other species in sluggish equilibrium.[7] (The shape of this "second" wave varies with the age of the solution: a similar dependence with the chromium(III) tartrates was described by Pecsok.[26] Because this was not realized at the time, a large volume of the alkaline copper tartrate solution was prepared and used intermittently over a period of several weeks. Hence the several polarograms of the pure solution shown are not superimposable. Data quoted for $E_{1/2}$ of this wave were secured from polarograms of specially prepared fresh solutions.) Even as little as $10^{-6}\%$ gelatin perceptibly changes the shape of the "hump" at −1.4 v., and with $1 \times 10^{-3}\%$ gelatin the height of the first wave is only 89% of its normal value. More gelatin causes a continued decrease in this wave height while the following coalesce and move to more negative potentials. When the first wave has completely disappeared, the $E_{1/2}$ of the "second" has moved from −0.94 v. to about −1.6 v., and finally becomes constant at −1.80 v. with $5 \times 10^{-2}\%$ gelatin or more.

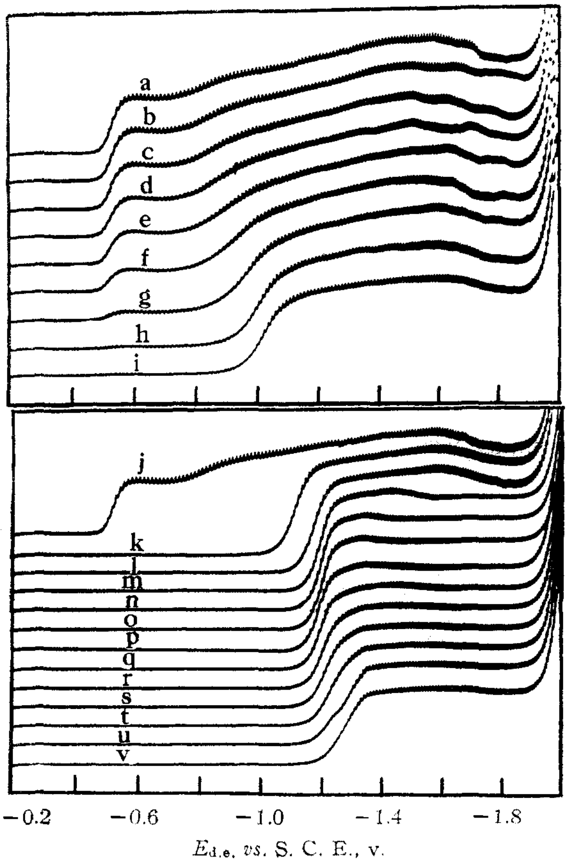

Fig. 12.—Polarograms of 4 mM copper (II) in 0.5 F potassium sodium tartrate-F potassium hydroxide with (a) 0, (b) 0.476, (c) 0.952, (d) 1.42, (e) 1.90, (f) 2.80, (g) 4.58, and (h) 7.97×10^{-5}; (i) 1.26, (j) 0, (k), 3.19, (l) 6.32×10^{-4}; (m) 1.00, (n) 1.60, (o) 2.72, (p) 5.22, and (q) 7.33×10^{-3}; (r) 1.34, (s) 1.93, (t) 2.52, (u) 3.07, and (v) 5.62×10^{-2} F sodium laurate.

Similar, though smaller, effects are found with sodium laurate (Fig. 12), myristate and lauryl sulfonate, dodecyl- and hexadecyltrimethylammonium bromides, gum arabic, gum ghatti, agar, Triton X-100 and methyl red. The effect of dodecyltrimethylammonium bromide on this $E_{1/2}$ is shown in Fig. 10b. Of the two discontinuities found here and with the hexadecyltrimethylammonium compound, that at the higher concentration is in the better agreement with the "critical concentration for micelle formation" found by other methods in salt-free solutions. The other is probably due to the influence of the highly charged anions present in these solutions. The two discontinuities found with the anionic materials parallel the two discontinuities found by Ekwall[27] from conductance measurements.

Discussion

Several examples of one or another of these classes have been described previously, and have generally been explained by one of two mechanisms. One of these[2] holds that they are due to complex formation, but this can hardly be held responsible for an effect taking place at a concentration of surface-active material which is substantially independent of the nature or concentration of the substance with which it is supposed to react. Further, taking a commonly accepted value[28] for the equivalent weight of gelatin, one calculates that, with 4 mM metal ion and an "average" polarographic critical concentration of gelatin of $5 \times 10^{-3}\%$, there would be seventy moles of metal per equivalent of gelatin. Correspondingly, with methyl red one would have to attribute these large effects to the formation of a complex containing a hundred or more metal ions per methyl red molecule.

Another explanation assumes the phenomena to be due to adsorption of the surface-active material on the surface of the mercury drop, and the discontinuity is explained by assuming that an "incubation time" is required for the orientation of the adsorbed material.[1,29] It is difficult to imagine an adsorption mechanism which is totally independent of the sign and charge of the double layer around the drop. But these effects occur with gelatin, for example, with waves having any $E_{1/2}$ between +0.03 and −1.6 v. Worse yet, they occur in cases where the "adsorbed" material is destroyed as fast as it reaches the electrode surface. Thus, methyl red is stable in neutral solutions only between −0.15 and −0.30 v., for it is both oxidizable and reducible at the dropping electrode, and outside this range of potentials it is not surface-active (Fig. 31b). As there can be no methyl red adsorbed on the electrode surface outside this potential range, it is peculiarly embarrassing to this theory to find the dye exerting an effect on the polarogram of, for example, cobalt(II) in a pyridine–pyridinium ion buffer, for which $E_{1/2} = -1.065$ v.

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(26) R. L. Pecsok, Ph.D. Thesis, Harvard University, 1948.

(27) P. Ekwall, *Kolloid-Z.*, **101**, 135 (1942).

(28) A. L. Ferguson, 5th Colloid Symposium Monograph, p. 157, 1928.

(29) B. Keilin, THIS JOURNAL, **70**, 1984 (1948).

In many cases, pronounced changes in the colors of solutions take place near the polarographic critical concentration. The normal deep blue of the hydroxytartrato-copper(II) complex is changed to greenish by dodecyltrimethylammonium bromide, while gelatin gives (as with the corresponding citrate complex) a light purplish-blue succeeded, at higher concentrations, by pure violet. Hexadecyltrimethylammonium bromide alters the light greenish-blue of the copper(II) hydrogen tartrate complex to a deep green. A pink solution of cobalt(II) in *F* potassium thiocyanate becomes blue on the addition of about $5 \times 10^{-3}\%$ Triton X-100, a color change long associated with the removal of water from cobalt (II) complexes.

While this strongly suggests some sort of reaction in the bulk of the solution, the observed polarographic effects vary so widely in nature, magnitude and direction as to make it appear that their complete interpretation must await a much more detailed study of the phenomena occurring both in the solutions and at the electrode surface.

The work here described was begun in collaboration with Dr. Eugene L. Colichman. It is a pleasure to acknowledge his coöperation and assistance in that portion of the experimental work dealing with the several copper tartrate systems.

Summary

When any of a number of surface-active materials is added to an aqueous solution, the drop time of a capillary producing approximately 4-sec. drops is substantially unaffected up to some sharply defined concentration, and then decreases nearly linearly with the logarithm of the concentration. The concentration at which the discontinuity occurs is identical with that at which the diffusion coefficient of methyl red suddenly decreases by a factor of about 100. Because these phenomena are closely similar to those characterizing the classical "critical concentration for micelle formation," this point is termed the "polarographic critical concentration."

Also occurring at this concentration are discontinuities in the effects of these materials on the polarograms of a wide variety of substances. The effects observed are divided into six classes. Two earlier explanations of isolated examples of these types of behavior are shown to be inadequate: a complete explanation will probably have to take into consideration both adsorption phenomena and direct or indirect (*i.e.*, activity effects) chemical reactions in the body of the solution.

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[30] Original manuscript received May 7, 1949.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Chain Reactions Induced by Enzymic Systems

BY GIUSEPPE PARRAVANO

Recent work on induced polymerization at catalytic surfaces[1] offered the opportunity to test whether enzymic and biological systems are able to initiate chain polymerization reactions of a vinyl monomer. This note describes some results obtained in this study.

Exploratory work was begun with the use of washed suspensions of *B. coli*. During formic acid decomposition by *B. coli* an aqueous solution of methyl methacrylate (MMA) was added, and turbidity detected in the system over a period of a few days, at room temperature. However, in view of the difficulties involved in the use of a living system work has been continued with pure enzymes.

The enzymatic reaction chosen was formaldehyde dehydrogenation by xanthine oxidase (Schardinger enzyme) (XO). The enzyme was obtained from fresh milk by the method of Dixon and Kodama.[2] Polymerization reactions were carried out in test-tubes filled with appropriate amounts of reactants, thoroughly degassed by high vacuum technique. Results are collected in Table I (MB = methylene blue; AN = acrylonitrile).

Experiments were made to ascertain the influence of oxygen on the system. For this purpose samples were prepared which were not degassed. Results are collected in Table II.

TABLE I

POLYMERIZATION INDUCED BY ENZYMATIC DEHYDROGENATION OF 0.4% SOLUTION FORMALDEHYDE, $t = 22°$

Enzyme soln., cc.	HCHO soln., cc.	MMA, cc.	MB, soln., cc.	Polymer ppts., hr.	Remarks
5	5	...	2	..	Color fades
4	5	0.2	..	$\sim$15	Two samples
6	5 (4%)	.3	..	$\sim$10	
2	1	.1	..	$\sim$24	+5 cc. H_2O
4	5	.2	1	$>$5 days	
4	.....	.2	..	No polymer	+5 cc. H_2O; two samples
4	5 (4%)	1 (AN)	..	$\sim$12	
16	10 (4%)	1.5	..	$\sim$2 days	

TABLE II

POLYMERIZATION INDUCED BY ENZYMATIC DEHYDROGENATION OF 0.4% FORMALDEHYDE SOLUTIONS, $t = 22°$, SOLUTION NOT DEGASSED

Enzyme soln., cc.	HCHO soln., cc.	MMA, cc.	MB soln., cc.	Remarks
4	5	...	1	Color does not fade
4	5	0.2	..	Some polymer after 5 days
4	5	.2	1	No polymer after 10 days
4	..	...	1	+5 cc. H_2O, color does not fade

Discussion

From the results of Table I it can be concluded

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[1] THIS JOURNAL, **72**, 3856 (1950).

[2] Dixon and Kodama, *Biochem. J.*, **20**, 1104 (1926).