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# Concerning the Effect of Surface-active Substances on Polarographic Currents

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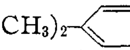
Surface-active materials have a marked effect upon electrode processes and a systematic investigation of various ways by which this action takes place in polarography is reported. Oscillographic current–time curves during the life of single mercury drops furnish considerably more information than usual polarograms and a detailed study of such curves allows an interpretation of the various types of phenomena encountered. The time delay usually observed before the surface-active material affects the electrode process is explained from the viewpoint of diffusion-controlled transport of the surface-active agent to the electrode and of the rate of its adsorption on the electrode. The inhibition of the electrode process, caused by the adsorption of the surface active material at the electrode, is discussed with chief attention devoted to the mechanism and kinetics of electrode reactions. The ideas presented readily can be extended to explain unusual polarographic waves observed in other cases, such as in electrode processes where insoluble, or strongly surface active, products of the electrode reaction are formed.

A large and increasing number of reports describe the striking influence of gelatin and other surface-active agents on polarograms, oscillographic polarograms, chronopotentiograms and other electrochemical processes. The effects vary widely, ranging from the shift of the polarographic half-wave potential, the decrease of limiting current, the appearance of minima, the splitting of a wave, to the complete elimination of a wave. Often no attempt is made to explain the origin or nature of these effects. At other times various, and in part contradictory, hypotheses have been presented to explain these effects.

This study was prompted as a result of an effect encountered in the amperometric titration of mixtures of metal ions with ethylenediaminetetraacetic acid.[1] The polarographic wave of ethylenediaminetetraacetato-bismuth(III) ion was decreased and eventually *completely* obliterated by the successive addition of small amounts of gelatin.

When such a distorted wave was recorded with a rapid response recorder, the current–time curves for the single drops showed peculiar shapes, *e.g.*, the drop fell at the bottom between the two recorded peaks and not on top of each peak as in the normal case.[2] Only a few examples of such "abnormal" current–time curves are reported in literature.[3–7] However, when polarograms of other species known to give distorted polarograms upon the addition of surface active substances, were recorded without damping in the presence of Triton X-100 (average formula $(CH_3)_3$-C-$CH_2$-C$(CH_3)_2$--($OCH_2$-$CH_2)_{9-10}$—OH) similar "abnormal" current–time curves were found indicating the *general* appearance of this type of current–time curve.

Recorded at high damping, the abnormal shape of individual current–time curves is hardly noticed with the result that valuable clues as to the proper interpretation of a distorted polarogram may be overlooked. It appeared that a detailed study of current–time curves would give some useful information concerning the mechanism of the effects of surface active substances observed in polarographic waves, as the latter are actually just the integral of current–time curves of single drops.

## Experimental

**Chemicals.**—All chemicals used were AR grade. Triton X-100 and some highly fractionated samples of octylphenoxyethanols ($OPE_{10.1}$) were obtained through the courtesy of Rohm and Haas Company, Philadelphia.

**Polarograms.**—Polarograms were recorded with a Leeds and Northrup Electrochemograph. The capillary had an $m$ value of 2.3 mg. sec.$^{-1}$ and a drop time of 3.6 sec. in 0.1 $M$ KCl at a height of the mercury reservoir of 50 cm. (closed circuit). The cell consisted of a 50-ml. beaker with a Lucite cover. The cell was surrounded by a condenser-type jacket connected in turn to a constant temperature bath maintained at 25.0 ± 0.1°. A saturated calomel electrode with an agar bridge served as a reference electrode. All potentials reported are referred to the SCE. For a run, 40 ml. of polarographic solution was placed in the cell and 0.4 to 2.0 ml. of solution of the surface active agent were added from a micro-buret. Thus the dilution would not exceed 5% and its effect on the polarograms could be considered negligible.

**Current–Time Curves of Single Drops.**—The same procedure as in the polarograms was applied but a slow dropping capillary was used for these measurements ($m$ = 0.95 mg. sec.$^{-1}$, $t$ = 6.3 sec.). The potential applied to the cell was taken from a Leeds and Northrup student potentiometer. The current was determined from the voltage drop across a 2000 Ω resistance. For recording, the voltage drop was first preamplified by a simple d.c. amplifier and then led into a Dumont Cathode-Ray Oscillograph, Type 350. The abscissa of the oscillographs was calibrated by a multivibrator impulse generator, the ordinate by a voltage applied from a potentiometer. Pictures of the oscillograms were taken with a Land Polaroid Camera, Model 95A.

## Results and Discussion

Figure 1 shows polarograms, recorded at high damping, of the ethylenediaminetetraacetato-copper(II) complex ion (Cu EDTA or $CuY^=$) at $p$H 3.5 with various amounts of Triton X-100 present. Over a considerable potential range the limiting current is strongly decreased by the Triton. Figure 2 represents oscillographic current–time curves for single drops (at a potential of −0.6 v. *vs.* SCE) corresponding to the polarograms (Fig. 1) with the various amounts of Triton X-100 present. Increasing concentration of the surface active agent terminates the electrode reaction (current drops to zero) at shorter and shorter time intervals. However, the curve always follows the pattern of the normal, diffusion-controlled current–time relationship during the initial growth of the drop. With eosin or gelatin, the same type of current–time

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(1) C. N. Reilley, W. G. Scribner and C. Temple, *Anal. Chem.*, **28**, 450 (1956).

(2) C. N. Reilley, "Proc. Symposium Trace Analysis," New York City, N. Y., 1955, in press.

(3) K. Wiesner, *Coll. Czech. Chem. Comm.*, **12**, 594 (1947).

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

(5) W. C. Davies and W. Furness, "Proc. 1st Int. Polarographic Congress," Vol. 1, Prague, 1951, p. 28.

(6) H. S. Campbell, *Trans. Faraday Soc.*, **50**, 1351 (1954).

(7) M. Dratovsky and M. Ebert, *Chem. Listy*, **48**, 498 (1954).

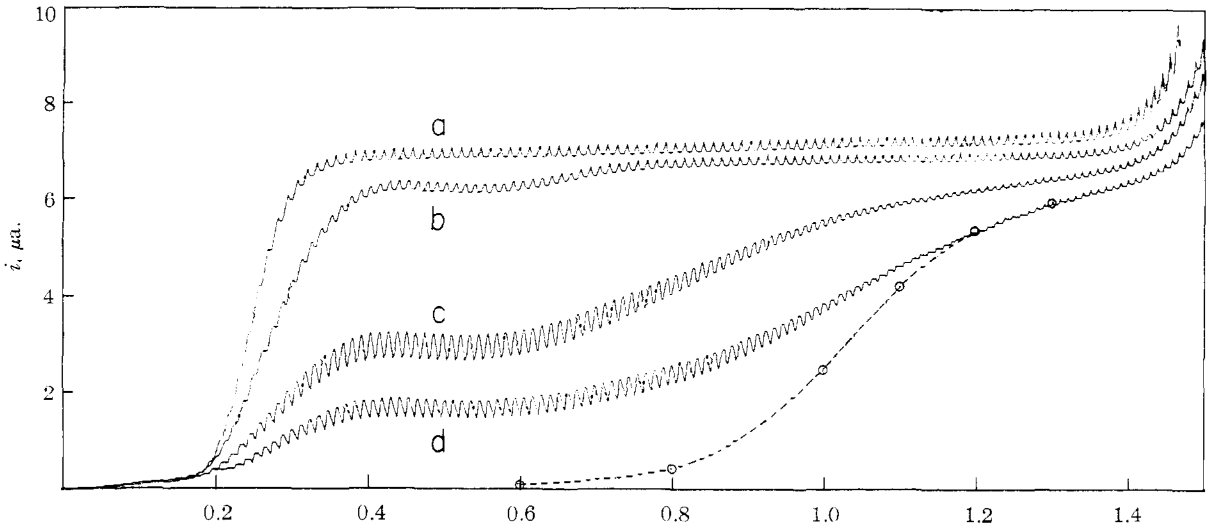

Fig. 1.—Distortion caused by addition of surface-active material. Polarograms of a solution containing 0.001 *M* CuEDTA, 0.009 *M* EDTA, 0.1 *M* tartrate buffer, *p*H 3.5 with various amounts of Triton X-100 present: (a) 0%; (b) 0.002%; (c) 0.003%; (d) 0.004%.

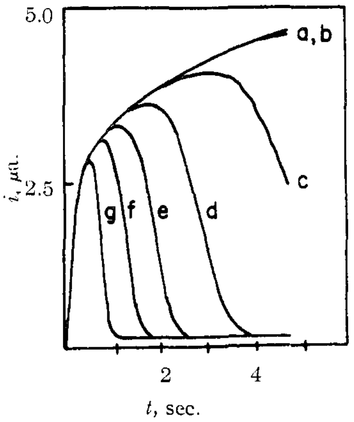

Fig. 2.—Inhibition of electrode reaction. Current–time curves for a single drop in the solution whose polarograms are given in Fig. 1: (a) 0%; (b) 0.001%; (c) 0.0015%; (d) 0.002%; (e) 0.0025%; (f) 0.003%; (g) 0.004%; Triton X-100 present; *E* = −0.6 v.

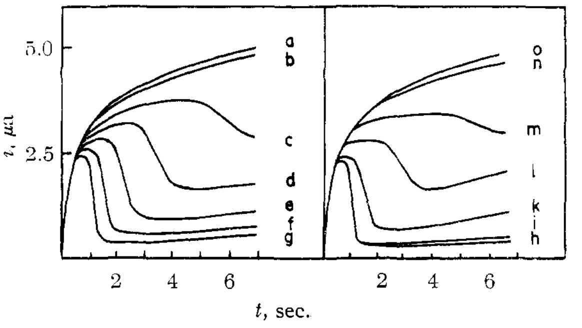

Fig. 3.—Surface coverage controlled by adsorption rate. Current-time curves for a solution containing 0.001 *M* CuEDTA, 0.009 *M* EDTA, 0.1 *M* acetate buffer, *p*H 4.6. Left drawing: *E* = −0.6 v. (a) 0; (b) 1.3 × $10^{-4}$, (c) 1.9 × $10^{-4}$; (d) 2.2 × $10^{-4}$; (e) 2.5 × $10^{-4}$; (f) 2.8 × $10^{-4}$; (g) 3.1 × $10^{-4}$ *M* camphor. Right drawing: 3.1 × $10^{-4}$ *M* camphor; (h) −0.6; (i) −0.7; (k) −0.8; (l) −0.9; (m) −0.95; (n) −1.0; (o) − 1.1 v.

curves was obtained. With camphor (Fig. 3, a-g) or 1-pentanol present, the current–time curves exhibited a different shape. Thymol, although qualitatively distorting the polarogram similar to Fig. 1, affected the current–time curves in a totally different way (Fig. 4).

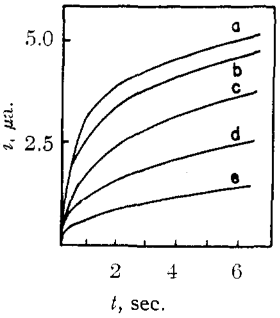

Fig. 4.—Surface coverage controlled by adsorption equilibrium. Current-time curves for a solution containing 0.001 *M* CuEDTA, 0.009 *M* EDTA, 0.1 *M* acetate buffer, *p*H 4.6: (a) 0; (b) 0.5 × $10^{-3}$; (c) 1.0 × $10^{-3}$; (d) 1.7 × $10^{-3}$; (e) 2.6 × $10^{-3}$ *M* thymol present. *E* = −0.6 v.

The influence of surface-active material on electrode reactions has been explained as a direct result of its adsorption on the electrode surface.[7-11] Accordingly, the extent of inhibition of a given electrode reaction during the life of a drop is related to the extent of coverage of the electrode surface through film formation. In addition, the effect of a given surface active substance on the polarographic wave is a function of the reducible species (Table I). Two main features were therefore considered, namely, the factors which control the ex-

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(8) M. Loshkarev and A. Kryukova, *Dokl. Akad. Nauk SSSR*, **62**, 97 (1948).

(9) S. L. Bonting and B. S. Aussen, *Rec. trav. Chim. Pays-Bas*, **73**, 455 (1954).

(10) J. Heyrovsky, F. Sorm and J. Foreijt, *Coll. Czech. Chem. Comm.*, **12**, 11 (1947).

(11) R. Tamamushi and T. Yamanaka, *Bull. Chem. Soc. Japan*, **28** 673 (1955).

tent and rate of film formation and those which influence the mechanism of inhibition of the electrode process.

## Factors Controlling the Extent of Film Formation

Surface coverage as a function of time depends on the adsorption coefficient, the rate constant of adsorption, the diffusion coefficient and the concentration of the surface active material. The adsorption coefficient and the adsorption rate are potential dependent. The simultaneous influence of these numerous parameters makes the interpretation of current–time curves in the presence of surface-active substances in general difficult. However, experimentally three extreme types of current–time curves may be distinguished, where the extent of film formation is governed *mainly* (1) by the rate of diffusion of the surface-active agent, (2) by the adsorption equilibrium, and (3) by the rate of adsorption and the adsorption equilibrium.

**Diffusion-controlled Film Formation.**—The current–time curves of Fig. 2 may be explained qualitatively in the following way[2]: from the instant of the formation of a new drop, surface-active material diffuses to the drop surface and adsorbs on it. In the initial period of the drop life, the amount of surface active material which has reached the surface by diffusion and has adsorbed on it is insufficient to retard the electrode reaction; consequently no deviation from the diffusion-controlled current occurs. Later in the drop life sufficient surface-active material has diffused to and absorbed on the expanding drop surface to produce a considerable deceleration of the electrode reaction rate. The current thus decreases and eventually reaches zero when the drop is completely covered with surface-active material. In other words, the rate of growth of the mercury drop surface compared to the rate of covering decreases during the life of a drop. The higher the concentration of the surface active material, the shorter is the time required to cover the drop.

The kinetics of film formation on a mercury drop have been derived with help of the Ilkovic equation taking diffusion as the rate controlling step[12]; this assumes that adsorption equilibrium is reached very rapidly and that the adsorption coefficient is very large. The time $\vartheta$, at which the surface is completely covered, is given by

$$\vartheta = 1.82 \times 10^6 \frac{\Gamma_s^2}{DC^2} \qquad (1)$$

where $\Gamma_s$ is the number of moles per cm.$^2$ mercury surface at surface saturation, $C$ is the bulk concentration of surface agent in moles/liter, $D$ is the diffusion coefficient of the surface active agent in cm.$^2$ sec.$^{-1}$. Thus, the time required to cover the surface completely with adsorbed material on a fresh mercury drop is inversely proportional to the *square* of the bulk concentration of the surface agent in solution.

Koryta,[12] in order to prove experimentally the diffusion-controlled nature of surface coverage using slow response current recording, derived a formula for the *average* current as a function of the concentration of surface-active agent and drop time. For simplifying the derivation, he assumed that the current suddenly vanishes at the instant when the surface is completely covered. However, as it can be seen from Fig. 8, such an approximation is by no means always justified.

The validity of equation 1 can be tested much more directly with oscillographic current–time curves by comparing $\vartheta$, the time when the surface of the drop is just covered, with $t^0$, the time when the current reaches zero. For this purpose current–time curves similar to Fig. 2 were obtained by addition of increasing amounts of eosin to a solution of copper-EDTA at *p*H 6.6. The time $t^0$ is found by extrapolating the descending branch of the curves linearly to zero current. The rounding, occurring in the region where the current reaches zero, is attributed to the adsorption rate which becomes increasingly important when the electrode surface is nearly covered with a monolayer of the surface-active agent. A plot of $t^0$ *versus* $1/C^2$ (where $C$ is the concentration of eosin) should, according to equation 1, yield a straight line going through the origin. Indeed, such a straight line was obtained (Fig. 5) with the slope of $5.8 \times 10^{-9}$ mole$^2$ sec. liter$^{-2}$. If $\vartheta$ does correspond to $t^0$, this slope should be equal to the coefficient, $1.82 \times 10^6\ \Gamma_s^2/D$, in equation 1 and the number of moles per cm.$^2$ $\Gamma_s$ can be calculated according to

$$1.82 \times 10^6 \frac{\Gamma_s^2}{D} = 5.8 \times 10^{-9}$$

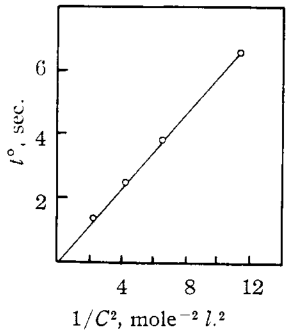

Fig. 5.—Time $t°$ of zero current at various concentrations of eosin.

Because eosin itself is reducible at the dropping mercury electrode, its diffusion coefficient could be determined polarographically using the Ilkovic equation. The value of $D$ obtained was $6.7 \times 10^{-6}$ cm.$^2$ sec.$^{-1}$, under the assumption that the wave is diffusion controlled and involves two electrons. Thus, a value of

$$\Gamma_s = 1.46 \times 10^{-10} \text{ mole cm.}^{-2}$$

was calculated. This corresponds to an area of 114 Å.$^2$ occupied per molecule of eosin. Kalousek and Blahnik[13] report from surface tension measurements a value of 106 Å.$^2$ per molecule of eosin. The agreement between these values lends support to the assumption that in this case diffusion governs the rate of covering the mercury drop with surface-active agent and that the time $t^0$, at which the current reaches zero also corresponds to the time $\vartheta$, at which the surface is completely covered.

(12) J. Koryta, *Coll. Czech. Chem. Comm.*, **18**, 206 (1953).

(13) M. Kalousek and R. Blahnik, *ibid.*, **20**, 782 (1955).

A linear relationship between $t^0$ and $1/C^2$ with an intercept of zero also was obtained with Triton X-100 and $\text{OPE}_{10.1}$ (a fractionated material, homolog to Triton X-100, with an average of 10.1 ethoxy groups) and for several other depolarizers. The slopes are of the same order of magnitudes as in the case of eosin. However, values of $\Gamma_s$ could not be calculated for the octylphenoxyethanols because their diffusion coefficients are not known.

The derivation of equation 1 given by Koryta can be extended easily to obtain the fraction $\theta$ of the surface covered at the time $t$. Thus

$$t = 1.82 \times 10^6 \frac{\theta^2 \Gamma_s^{\,2}}{DC^{02}} \tag{2}$$

Because $t^0$ is equal to $\vartheta$, the fraction of surface covered $\theta$ can be calculated easily as a function of time, when $t^0$ for a given surface agent concentration has been measured

$$\theta = \sqrt{\frac{t}{t^0}} \tag{3}$$

**Surface Coverage Limited by Adsorption Equilibrium.**—The above statements apply only for strongly surface active substances, *i.e.*, for those whose thermodynamic adsorption equilibrium, even at the smallest concentration employed, allow essentially complete coverage of the surface. With weaker surface active agents, different results are obtained. For example, when an alcoholic solution of thymol[14] is added to a copper-EDTA solution, a decrease in reduction current is obtained and the gross polarographic current–potential relationship resembles Fig. 1. However, the current–time curves in this case (Fig. 4) are quite different from those illustrated in Fig. 2. Considerably higher *molar* concentrations of thymol ($\sim$ 30 × that of Triton X-100 or eosin) had to be present in order to cause a decrease in diffusion current. The deviation from the normal diffusion-controlled current-time curve occurred practically from the *beginning* of the drop life, unlike the deviation observed when Triton X-100 or eosin were employed. Assuming the surface concentration at saturation equal to $10^{-9}$ mole/cm.$^2$ and the diffusion coefficient as $10^{-5}$ cm.$^2$ sec.$^{-1}$, then, according to equation 1, complete surface coverage could be attained within only $2 \times 10^{-4}$ second for this concentration of $10^{-3}$ mole/liter thymol present in solution. However, the adsorption coefficient is not sufficiently large to cause a complete coverage of the surface at this concentration of thymol. Practically from the instant of its formation the mercury drop will be partially covered with an equilibrium concentration of thymol.

The fraction of the surface covered is the *same* throughout the life of the drop and this fraction will increase as the concentration of surface-active material in the bulk phase increases. The curves of Fig. 4 correspond to various points in a Langmuir isotherm. With increasing concentration of thymol the current not only decreases, but the curve shape changes successively from a $t^{1/6}$ to a $t^{2/3}$ relationship. As a result the polarographic limiting current becomes successively more independent from the height of the mercury reservoir as more thymol is employed. The current in the presence of $2.6 \times 10^{-3}$ $M$ thymol (curve e in Fig. 4) thus behaves as a kind of kinetic current. At potentials more negative than $-0.6$ v. the polarographic current rises again and at $-1.0$ reaches it full height. An electrocapillary curve shows that thymol desorbs in this potential region. The current–time curves in the region of desorption are similar to the curves in Fig. 4. An increase of potential from $-0.6$ to $-1.0$ gradually changes the current time curve e to the shape a (in the presence of $2.6 \times 10^{-3}$ $M$ thymol). In other words, the current–time curves exhibit the same qualitative shape whether desorption is caused by decreasing the thymol concentration or by increasing the negative potential.

**Surface Coverage Limited by Adsorption Rate and Adsorption Equilibrium.**—Camphor depresses the wave of copper-EDTA strongly within the potential region where camphor is adsorbed (about $-0.3$ to $-1.0$ v.). Figure 3a-g illustrates the influence of increasing amounts of camphor on the current–time curves of copper-EDTA at *p*H 4.6 and at $-0.6$ v. The current deviates from the diffusion-controlled value long before reaching the maximum and drops to zero only at higher camphor concentrations.

Assuming $\Gamma_s$ equal to $10^{-9}$ mole/cm.$^2$ and $D$ equal to $10^{-5}$ cm.$^2$ sec.$^{-1}$, the $\vartheta$ values obtained from equation 1 at the camphor concentrations employed are of the same order of magnitude as the experimentally found values of $t^0$. However, a plot of $t^0$ *vs.* $1/C^2$ does not give a straight line, but bends upward. It can therefore be assumed that the camphor at lower concentrations does not adsorb at the electrode surface as fast as it arrives and that the adsorption *rate* takes part in controlling the velocity of the surface coverage. This assumption is further supported in the following way.

The curves h-o in Fig. 3 show the effect of increasing the negative voltage up to the desorption potential of camphor ($-1.0$ v.); in this case $3.1 \times 10^{-4}$ $M$ camphor is present. Curves g and h of Fig. 3 are identical. *Decreasing the camphor concentration and increasing the potential have a similar effect on the current–time patterns.* In both cases the adsorption rate is decreased (or the desorption rate increased) and the adsorption equilibrium is shifted toward desorption. The curves at intermediate conditions of potential or concentration show a second current rise, which corresponds approximately to a steady-state concentration of camphor at the mercury surface.

With the highest camphor concentration employed ($3 \times 10^{-4}$ $M$) and at the potential of strongest adsorption (around $-0.6$ v.), a potential change of 0.1 v. (curves h and i) has practically no influence on the current–time curve. This implies that under this particular condition the adsorption rate is fast compared with the rate of diffusion. The surface coverage is then diffusion-controlled and the adsorption equilibrium is shifted toward complete adsorption.

Addition of alcohol changes considerably the current–time curves obtained in the presence of

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[14] Without alcohol present the same type of curve is obtained in this case.

TABLE I

EFFECT OF TRITON X-100 (0.004%) AND GELATIN (0.04%) ON POLAROGRAPHIC WAVES OF VARIOUS METAL IONS AND COMPLEXES

Concentration of metal $10^{-3}$ $M$, supporting electrolyte $10^{-1}$ $M$

| Metal | Supporting electrolyte | Species predominantly present | Effect of gelatin | Effect of Triton X-100 |
|---|---|---|---|---|
| Cd | $KNO_3$ | $\mathrm{Cd}^{++a}$ | No | Irreversibility |
| Cd | KCNS | $\mathrm{Cd}^{++} + [\mathrm{CdCNS}]^{+b}$ | No | No |
| Cd | $NH_3/NH_4NO_3$, $p$H 9.3 | $[\mathrm{Cd(NH_3)_4}]^{++c}$ | No | Irreversibility |
| Cd | $KNO_3$ + ethylenediamine | $[\mathrm{Cd(en)_3}]^{++d}$ | No | Slight irreversibility |
| Cd | Triethylenetetramine in phosphate buffer $p$H 7.3 | $[\mathrm{Cd\ trien}]^{++c}$ | Slight irreversibility | Irreversibility |
| Cu | $NaNO_3$ | $\mathrm{Cu}^{++}$ | No | Slight depression |
| Cd | KCl | $[\mathrm{CdCl}]^{+e}$ | No | Irreversibility |
| Cd | Tartrate buffer $p$H 3.5 | $[\mathrm{Cd\ Tart}]^{0c}$ | Irreversibility med. depression | Irreversibility medium depression |
| Cu | Tartrate buffer $p$H 4.0 | $[\mathrm{Cu\ Tart}]^{0c}$ | Slight depression | Strong depression |
| Cu | $Na_2SO_4$ | $[\mathrm{CuSO_4}]^{0f}$ | No | Strong depression |
| Cd | Citrate buffer $p$H 5.4 | $[\mathrm{Cd\ Citr}]^{-c}$ | Irreversibility | Strong depression |
| Cd | KCN | $[\mathrm{Cd(CN)_4}]^{-2g}$ | Strong depression | Strong depression |
| Cu | EDTA in acetate buffer $p$H 4.6 | $[\mathrm{Cu\ EDTA}]^{-2c}$ | Strong depression | Strong depression |
| Zn | $K_2C_2O_4$ | $[\mathrm{Zn(Ox)_3}]^{-4h}$ | Strong depression | Strong depression |

[a] I. Leden, *Z. physik. Chem.*, A188, 160 (1941). [b] D. N. Hume, D. D. DeFord and G. B. C. Cave, THIS JOURNAL, **73**, 5323 (1951). [c] A. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice–Hall, Inc., New York, N. Y., 1952. [d] B. E. Douglas, H. A. Laitinen and J. C. Bailar, THIS JOURNAL, **72**, 2484 (1950). [e] M. Strocchi, *Gazz. chim. ital.*, **80**, 234 (1950). [f] S. Fronaeus, *Acta Chim. Scand.*, **4**, 72 (1950). [g] H. Gerischer, *Z. Elektrochem.*, **57**, 604 (1953). [h] H. Gerischer, *Z. physik. Chem.*, **202**, 302 (1953).

camphor. The current in the *later* part of the drop life is increased by this addition. The phenomenon is attributed to a change in the adsorption equilibrium.

### Inhibition of Electrode Process by a Surface Film

In Table I the influence of Triton X-100 and of gelatin on a number of metal ions and metal complexes is listed under conditions in which the surface-active agents are present at such concentrations that surface coverage is achieved within about the same time for both surface-active agents. First, it can be noticed that Triton X-100 in general has a stronger influence on the electrode reactions than gelatin. A possible explanation for this difference may lie in the fact that the Triton X-100 consists of smaller, more similar molecules of approximately the same molecular weight. Gelatin on the other hand is a higher molecular weight material with a broader distribution of size and structure. The structure of the interface may therefore be more tightly packed in the case of Triton X-100 than in the case of gelatin and thus have a stronger effect on the electrode reaction.

Secondly, the degree of inhibition by the surface-active agent depends markedly upon the particular reducible species.[15] A thorough discussion of this selectivity would require a detailed knowledge of the steps involved in these electrode reactions. However, such detailed reaction mechanisms are known for only a very limited number of electrode reactions.[16,17]

An electrode process at a mercury or an amalgam electrode may generally be divided into (a) transportation processes, (b) chemical reactions prior to and after the discharge, (c) the electron transfer reaction itself. Accordingly, three and at times contradictory theories have been put forward, claiming an inhibited penetration ("sieve" theory),[8,18,19] inhibited chemical reaction[10,20–22] or a decelerated electron transfer[23–26] by a film of adsorbed surface active material at the electrode surface.

**Inhibited Penetration, The "Sieve Theory."**—The data from Table I show that the steric factors assumed in the "sieve theory"[18,19] cannot satisfactorily account for the sequence of the selective effect of the surface-active agent toward different reducible particles. For example, the limiting current of the comparatively large ion $[\mathrm{Cd\ (en)_3}]^{++}$ is not decreased by gelatin or Triton X-100, whereas the limiting current of the smaller $[\mathrm{Cd(CN)_4}]^{--}$ is strongly decreased. Furthermore, steric factors cannot easily explain the widely different degrees to which the limiting currents of CdEDTA, Pb-

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(15) The supporting electrolyte may exert a competition with the surface active material for the electrode surface, and as a result the steady-state concentration of Triton X-100 or gelatin would be slightly different in different media. Furthermore, the equilibrium concentration of adsorbed surface-active material is potential dependent. It is possible that, in some cases, the different behavior of the reducible ions of Table I is due to these effects. Notwithstanding, the sensitivity of a wave toward the surface active material is primarily a function of the electrode reaction. This assumption is supported by the different behavior of the EDTA complexes of cadmium, lead and bismuth toward Triton X-100 under identical conditions (Fig. 6).

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(18) A. G. Stromberg and M. S. Gutermann, *Zhur. Fiz. Khim.*, **27**, 993 (1953).

(19) H. Imai and S. Chaki, *Bull. Chem. Soc. Japan*, **29**, 498 (1956).

(20) J. Heyrovsky, *Disc. Faraday Soc.*, **1**, 212 (1947).

(21) J. Heyrovsky and M. Matyas, *Coll. Czech. Chem. Comm.*, **16**, 455 (1951).

(22) J. Heyrovsky, *ibid.*, **19**, suppl. II, 58 (1954).

(23) A. N. Frumkin, *Dokl. Akad. Nauk SSSR*, **85**, 373 (1952).

(24) A. P. Martirosyan and T. A. Kryokova, *Zhur. Fiz. Khim.*, **27**, 851 (1953).

(25) J. E. B. Randles, *Disc. Faraday Soc.*, **1**, 11 (1947).

(26) J. E. B. Randles and K. W. Somerton, *Trans. Far. Soc.*, **48**, 937, 951 (1952).

EDTA and BiEDTA are affected by Triton X-100 (Fig. 6), for these three complex ions certainly are nearly of the same size. The experimental results obtained in this study are thus hardly compatible with the concept of inhibited penetration.

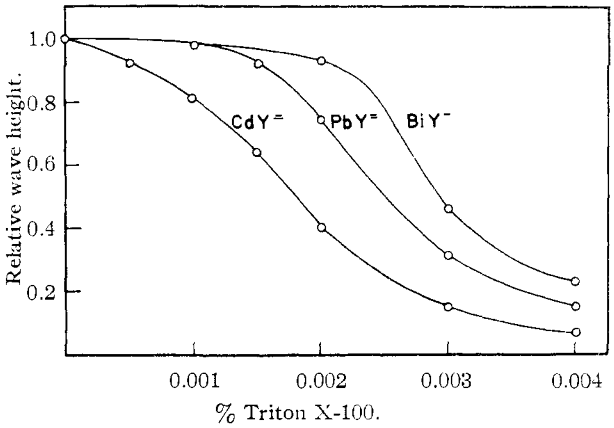

Fig. 6.—Relative depression of polarographic waves of metal EDTA complexes (0.001 *M* M-EDTA, 0.004 *M* EDTA) in 0.1 *M* tartrate buffer, *p*H 3.5 by Triton X-100; *E* = −1.25 v.

**Deceleration of Electron Transfer.**—In a number of the cases listed in Table I, the reduction waves became only more drawn out (more "irreversible") by addition of surface active agent. In other cases severe depressions of the polarograms similar to Fig. 1 occurred. Both types of distortion may be the result of a retarded electron transfer reaction, the deceleration occurring to different extents. A film of surface active material causes severe changes in the conditions present at the electrode-solution interface such as displacement of adsorbed ions and water molecules, changes in the dielectric constant and a different geometrical positioning of the reducible species at the electrode surface. As a result the electron transfer is decelerated. Figure 7 shows current-time patterns in a case where "irreversibility" of a polarogram is produced by $OPE_{10\cdot 1}$. If a current-potential diagram is constructed from Fig. 7 for a certain time value (dotted line, corresponding to a definite drop area) a slightly drawn out wave is obtained with a half-wave potential 50 mv. more negative than the half-wave potential in the absence of $OPE_{10\cdot 1}$. The current rise caused by the potential increase is a result of the *reaccelerated* irreversible electron transfer, thus indicating that it is actually the electron transfer rate which had been decreased by the surface active material.[27]

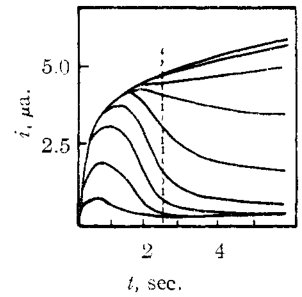

Fig. 7.—Reacceleration of electron transfer rate. Current–time curves for a solution of 0.001 *M* Cu-trien, 0.004 *M* trien (= triethylenetetramine), 0.1 *M* acetate buffer, *p*H 4.6, 0.003% $OPE_{10\cdot 1}$. Voltage for the curves from bottom to top: −0.20, −0.25, −0.30, −0.35, −0.40, −0.45, −0.50, −0.60, −0.70.

**Inhibition of a Chemical Step.**—From the examples listed in Table I it can be seen that the polarograms of reducible species carrying negative charges are more likely to suffer a decrease in limiting current by the surface active substance than the polarograms of reducible species carrying positive charges. Uncharged particles are in an intermediate position.

This charge effect appears related to a general mechanism in the reduction of complex ions: A negative species must acquire, by a chemical reaction step, a less negative charge before the electron transfer from the electrode to the species may occur. This reaction step may consist of the loss or gain of charged ligands or formation of an ion pair by reaction with an oppositely charged particle. In the case of the zinc oxalate and cadmium cyanide complexes, for example, the complexes predominantly present in solution are $[Cd(CN)_4]^{--}$ and $[Zn(Ox)_3]^{----}$, but the complexes discharged are $[Cd(CN)_3]^-$ and $[Zn(Ox)]$.[28,29] Metal-EDTA complexes may also have to detach some ligands prior to the discharge. The ligand may be more readily detached if a proton is added, a reaction which also reduces the negative charge.

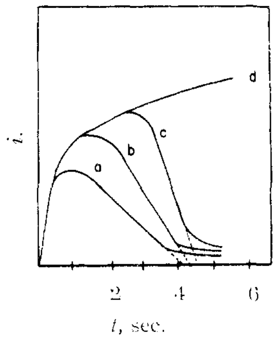

Fig. 8.—Effect of rate of electrode reaction. Current–time curves of (a) CdEDTA; (b) PbEDTA; (c) BiEDTA (0.001 *M* M-EDTA, 0.004 *M* EDTA) in 0.1 *M* tartrate buffer, *p*H 3.5, in the presence of 0.002% Triton X-100: (d) pattern in the absence of Triton X-100.

In the presence of surface-active agents, the usual "free" surface available for reactions which take place *at the electrode surface* decreases with a resulting increase in the effective current density. This situation demands more from the rates of chemical reactions and, as a result, electrode reactions which normally proceed at rates controlled by diffusion will commence to decrease in the pres-

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(27) In this potential region the adsorption equilibrium *increases* toward the more negative potentials. In cases (Fig. 1) where a current increase occurs on the negative side of the electrocapillary maximum, desorption and/or electron transfer reacceleration may be involved but these two factors cannot be distinguished from the experimental data.

(28) H. Gerischer, *Z. Elektrochem.*, **57**, 604 (1953).

(29) H. Gerischer, *Z. physik. Chem.*, **202**, 302 (1953).

ence of a surface film. This charge effect indicates that surface active substances cause a decrease in limiting current predominantly in those cases where a chemical reaction takes place prior to the electron transfer. However, the experimental results in this study do not affirm conclusively the inhibition of chemical reaction steps by surface active substances.

In order to investigate the effect of Triton X-100 on the reduction of similar compounds, polarograms of the cadmium, lead and bismuth complexes with EDTA have been recorded in a tartrate buffer of *p*H 3.5. The waves of all three compounds were easily obliterated by addition of Triton X-100. Figure 6 shows the relative effect of Triton X-100 on the average current at $-1.25$ volt. Increasing amounts of Triton X-100 were necessary to affect the reduction wave of cadmium-EDTA, lead-EDTA and bismuth-EDTA, respectively. Figure 8 shows the current–time curves for the three complex ions in the presence of 0.002% Triton X-100. The ordinate of the three curves has been normalized because of the different diffusion current constants involved in the reductions. It is evident from the diagram that the main difference between the three complexes is the time at which deviation from the diffusion controlled curve starts and the rate at which the current decreases as the surface becomes covered. The time at which zero current is reached is approximately equal for all three cases. This is the time when the surface first becomes completely covered.

The inhibited step of the electrode reaction is assumed to be either the electron transfer reaction or a conversion into electroactive form prior to the electron transfer, the reaction taking place at the electrode surface. Its reaction rate $v$ is, following the theory of heterogenous reactions, proportional to the concentration, $C_A$, of the reactant at the surface and the active (uncovered) surface

$$v = kC_A(1 - \theta(t)) \qquad (4)$$

where $\theta(t)$ is the covered fraction of the surface at time $t$. The reaction rate $v$ decreases with time as the surface becomes more extensively covered with the surface film. In the early stages of growth of the drop diffusion limits the current. When the electrode reaction rate has decreased to a critical value, the current commences to deviate from its diffusion-controlled course and decreases eventually reaching zero when $\theta(t)$ equals 1 and $v$ becomes 0. The larger the value of the rate constant $k$, the more extensively the surface has to be covered in order for the reaction rate to decrease to the critical value. Thus the rate constants probably increase in the order CdEDTA < PbEDTA < BiEDTA.

## Inhibition of Electrode Reactions by a Reaction Product

In certain cases, the product of electrolysis is insoluble or strongly surface active. Such products then accumulate on the electrode surface during the drop life and give rise to phenomena similar to those produced by added surface active agents—decrease in limiting current, appearance of two waves, sway-backed polarographic waves, etc.

For example, in a supporting electrolyte of 1 $M$ $NH_4Cl + 6$ $M$ $NH_3$, sodium vanadate shows a single wave up to a concentration of about $5 \times 10^{-4}$ $M$; at higher concentrations a double wave appears. The total wave height is proportional to the vanadate concentration, the height of the first wave remaining approximately independent of the vanadate concentration. The current–time curves at potentials for the prewave show an initial steep current rise, the current then passing through a maximum and finally decreasing according to a $t^{-1/3}$ function. This is the behavior expected when the current is proportional to the rate of growth of the electrode surface $[d(mt)^{2/3}/dt \propto (mt)^{-1/3}]$. The gross effect is identical in form but *different in mechanism* to the prewaves encountered in the reduction of reversible systems, such as methylene blue where the reduction product is strongly surface active and facilitates the reduction of the dye.[30] The inhibition mechanism is the only logical choice in the vanadate case because the second (main) wave was found to be *irreversible*.

At a vanadate concentration where the second wave was 5 times higher than the prewave, a reciprocal slope of 0.069 v. was obtained in a plot of $\log(i_d - i)/i$ *vs.* potential for the upper part of the second wave. Yet the wave height corresponds to the consumption of two or three electrons. In the reduction of such an irreversible system an adsorption of the reduction product cannot cause a prewave by *facilitating* the reduction process because no true electrode equilibrium is present between the oxidized and the reduced forms. The double wave is therefore assumed to be the result of an *inhibited* electrode reaction, the inhibition being caused by a surface film due to a reduction product which in this case is probably a vanadium hydroxide of lower valence state. In addition, the current shows fast and irregular oscillations of small amplitude, the oscillations being attributed to a periodic breaking of the film which probably is of crystalline structure. The current–time curves of the second wave are normal. In this potential region the inhibiting reduction product is either further reduced or it is no longer adsorbable.

The polarographic reduction of species of the type $M_xO_y^{-n}$ quite often yields double waves and in their interpretation the inhibition mechanism should be kept in mind. It is obvious that any thermodynamic interpretation of the first wave (such as determination of stable intermediate oxidation states from the relative heights of the two waves) would be erroneous.

## Electrochemical Masking

Under certain conditions the diffusion currents of a metal ion in the presence of the EDTA complex of another metal ion are not additive.[31] For example, in a mixture of bismuth-EDTA and lead ion, the bismuth-EDTA yields at more positive potentials, a wave which obeys the Ilkovic equation. The diffusion current of the lead wave, however, is not linearly dependent on the lead concentration. This phenomenon is a result of the back-

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(30) R. Brdicka, *Z. Elektrochem.*, **48**, 278 (1942).

(31) M. C. Bennett and W. S. Wise, *Trans. Faraday Soc.*, **52**, 696 (1956).

diffusion of the EDTA liberated in the reduction of the bismuth-EDTA. The freed EDTA combines with the lead to form non-reducible lead-EDTA, thus decreasing its diffusion current. Direct proportionality of the diffusion current on the lead ion concentration may be achieved by obliterating the reduction wave of bismuth-EDTA by adding Triton X-100. This technique, known as *electrochemical masking*, is therefore useful in such cases. In amperometric titrations of two-component mixtures electrochemical masking also allows enhanced measurement sensitivity.[1]

### Optimum Concentration of Maxima Suppressors

It should be realized that the concentration of surface active material which is recommended in textbooks for maxima suppression, *e.g.* 0.002% Triton X-100, is sufficient to produce a small distortion of the current–time curves for many depolarizers, especially when capillaries whose drop times exceed 4 seconds are employed. The optimum concentration will depend upon several factors such as the kinetics of the electrode process, the drop time of the capillary as well as the "activity" and diffusion coefficient of the surface active agent.

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[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

# Adsorption Kinetics and Electrode Processes. II

BY PAUL DELAHAY AND ISAAC TRACHTENBERG[1,2]

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The effects of adsorption of non-reducible (non-oxidizable) foreign substances on kinetic parameters for electrode reactions and limiting currents are discussed. The decrease in effective area and the variations of kinetic parameters (the rate constant $k_s$ at the standard potential and the transfer coefficient) resulting from adsorption can be separated when electrode coverages are determined. Coverages are obtained from measurements of the double layer differential capacity in the absence of the reducible (oxidizable) species. Application is made to the system Ti(IV)–Ti(III) in tartaric medium in presence of *n*-amyl alcohol, cyclohexanol or thymol. The rate constant $k_s$ is essentially independent of coverage ($\theta < 0.4$) for the first two substances and decreases markedly for thymol. The effect of adsorption on limiting currents is studied by polarography, electrode coverages during drop life being determined from measurements of the double layer differential capacity. Variations of the limiting current with coverage at the end of drop life are studied for several systems and a tentative explanation is advanced. The interpretation of complete waves which are complicated by adsorption of a foreign substance is discussed, and application is made to the cadmium wave in presence of *n*-hexyl alcohol. Experimental methods are discussed in some detail, and an extrapolation method for minimization of contamination effects is discussed. It is recommended that the dropping mercury (or amalgam) electrode be used in kinetic studies rather than the stationary hanging mercury (or amalgam) drop. Values of $k_s$ obtained with both electrodes are given for the $Cd^{++}$–Cd(Hg) system at 0°.

## Introduction

Three groups of problems arise in the study of the effects of adsorption on electrode processes: (a) influence of adsorption in the absence of electrode reaction, *i.e.*, adsorption on ideally polarized electrodes; (b) influence of the adsorption of foreign substances (not reduced or oxidized) on the rate of electrode reactions; and (c) influence of adsorption of the reducible and/or reduced species on the characteristics of electrode reactions involving these substances. We shall be concerned primarily with the first two problems in this investigation.

The first group of problems includes two broad studies, namely, the investigation of adsorption equilibria and the kinetics of adsorption. Adsorption equilibria at electrodes were studied some thirty years ago by Frumkin[3] and Butler[4] and recently by Hansen and co-workers.[5] It is observed that the surface concentration exhibits a maximum in the neighborhood of the electrocapillary maximum and, in general, approaches zero at sufficiently anodic (displacement by anions) and cathodic (displacement by the solvent such as water) potentials. Adsorption kinetics with mass transfer control were studied in some detail in this Laboratory.[6] It was shown that adsorption equilibrium is reached slowly (after 15–30 min.) in unstirred dilute solutions for concentrations in the segment of the isotherm that can be linearized as a first approximation.

The second group of problems, namely, the effect of foreign substances on the rate of electrode processes, involves two major studies: the effect of adsorption on kinetic parameters for the electrode reaction and the influence of adsorption on electrode processes controlled by mass transfer (effect on limiting currents or transition times). Coverage of the electrode by a foreign substance increases the effective current density and, consequently, the overvoltage. Furthermore, the kinetic parameters for the electrode reaction also can be affected, and this effect also causes a variation of overvoltage.

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[1] Predoctoral fellow, 1955–1957; American Oil Company, Research Department, Texas City, Texas.

[2] A preliminary report on this work was presented at the National Meeting of the Electrochemical Society, San Francisco, April, 1956.

[3] A. N. Frumkin, *Z. Physik*, **35**, 792 (1926).

[4] J. A. V. Butler, *Proc. Roy. Soc.* (*London*), **122A**, 399 (1929).

[5] R. S. Hansen, R. E. Minturn and D. A. Hickson, *J. Phys. Chem.*, **60**, 1185 (1956).

[6] P. Delahay and I. Trachtenberg, THIS JOURNAL, **79**, 2355 (1957).