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SECONDARY REACTIONS IN CONTROLLED POTENTIAL COULOMETRY. III. PRECEDING AND SIMULTANEOUS CHEMICAL REACTIONS

Allen J. Bard, and Emanuel Solon

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of phenol at the mercury–base solution interface. The parameter V_N of eq. 3 then was established to best represent the capacitance data near the polarization of maximum adsorption for given solute activity. From eq. 5 we obtain

$$\left(\frac{\partial \Gamma}{\partial V}\right)_a = \frac{1}{RT}\left(\frac{\partial Q}{\partial \ln a}\right)_V = \frac{1}{RT}\left(\frac{\partial Q}{\partial \Gamma}\right)_V\left(\frac{\partial \Gamma}{\partial \ln a}\right)_V \tag{43}$$

i.e., $(\partial \Gamma/\partial V)_a = 0$ when $(\partial Q/\partial \Gamma)_V = 0$. If Q is linear in Γ the potential at which $(\partial \Gamma/\partial V)_a = 0$ should be independent of Γ (and so of a), and if Frumkin's assumption as indicated by eq. 38 were valid, the potential of maximum adsorption should be $V_{max} = -C'V_N/C_w - C'$ (independent of a). In our earlier work it was noted that such constancy of V_{max} was not always observed; in the present work Q was found to be linear in Γ for n-amyl alcohol but not strictly so for phenol. Finally, the parameter S was established by (essentially) fitting the curvature of plots of θ_{app} against polarization in the neighborhood of the plot maxima. From eq. 43 we have

$$\frac{\partial^2 \Gamma}{\partial V^2} = \frac{1}{RT}\frac{\partial^2 Q}{\partial V \partial \ln a} = \frac{1}{RT}\left(\frac{\partial C}{\partial \ln a}\right)_V \tag{44}$$

and so

$$\frac{\partial^2 \theta}{\partial V^2} = \frac{S}{RT}\left(\frac{\partial C}{\partial \ln a}\right)_V \tag{45}$$

Equation 45 implies a relation between curvature of a plot of θ_{app} against V and molar area at full coverage, but does not furnish a basis for calculation of molar area from capacitance data alone. This is because $\partial^2\theta_{app}/\partial V^2$ differs strongly from $\partial^2\theta/\partial V^2$ even near the electrocapillary maximum where to good approximation $\theta = \theta_{app}$. It therefore appears impractical to avoid a model in calculation of molar area if double integration of capacitance curves is to be avoided. Choice of molar area to provide representation of curvature of plots of θ_{app} against V near their maxima must be considered to give only an approximation to this parameter if dependence of Q on Γ is not known to be linear, and results obtained with phenol in the present work show that such linearity cannot be assumed safely.

SECONDARY REACTIONS IN CONTROLLED POTENTIAL COULOMETRY. III. PRECEDING AND SIMULTANEOUS CHEMICAL REACTIONS

By ALLEN J. BARD AND EMANUEL SOLON

*Department of Chemistry, The University of Texas, Austin 12, Texas*

Controlled potential coulometric experiments, in which the electroactive species, C, is consumed before and during the electrolysis by a first- or second-order chemical reaction, or in which C is produced by a reversible chemical reaction preceding the electrode reaction, are considered. A mathematical treatment of the effect of these upon n_{app}, the apparent number of faradays per mole of electroactive material, and upon current–time behavior, is given. The use of controlled potential coulometric data for the estimation of the rate constants of the chemical reactions is described and several examples are given.

Introduction

Secondary chemical reactions during controlled potential coulometric electrolyses generally lead to variations in n_{app}, the apparent number of faradays per mole of electroactive substance consumed, and variations in the current–time behavior. Previous communications treated cases involving reactions of the product of the primary electrode reaction leading to consumption or regeneration of the electroactive species[1] or leading to secondary electrode reactions.[2] This paper discusses cases in which the electroactive species is consumed before and during the electrode reaction in a chemical reaction, and in which the electroactive species is produced by a reversible chemical reaction. The use of controlled potential coulometric data for the determination of the number of electrons involved in the electrode reactions and for the estimation of the rate constants of chemical reactions is described.
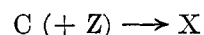
Classification.—The primary electrode reaction is represented as
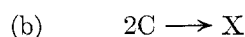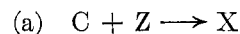
$$C \pm ne^- \longrightarrow R$$
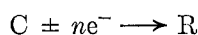
where C is the electroactive material and R is the product of the electrode reaction. In the reactions below

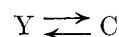R, X, Y, and Z represent electrolytically inert materials at the applied potential.

Case I. C Undergoes a Pseudo First-Order Chemical Reaction.—

$$C (+ Z) \longrightarrow X$$

Case II. C Undergoes a Second-Order Chemical Reaction.—

(a) $C + Z \longrightarrow X$

(b) $2C \longrightarrow X$

Case III. C is Produced by a Preceding, Reversible First-Order Reaction.—

$$Y \rightleftarrows C$$

Variations of these cases can be treated by suitable modification of the procedure outlined below.

Mathematical Treatment

General Considerations.—The assumptions and conditions of this treatment are the same as those previously described.[1,2] The current, i, taken as a positive quantity, is related to the rate of consumption of C by

$$i = -nFV[\mathrm{d}(C)/\mathrm{d}t]_{\text{elec. rxn.}} \tag{1}$$

(1) D. H. Geske and A. J. Bard, *J. Phys. Chem.*, **63**, 1057 (1959).
(2) A. J. Bard and J. S. Mayell, *ibid.*, **66**, 2173 (1962).

where F is the faraday, V is the total volume of solution, and (C) is the concentration of species C. The rate of concentration change under limiting current conditions (it is assumed that the applied potential is such that the electrode reaction occurs without activation polarization) is

$$[d(C)/dt]_{elec.\ rxn.} = -p(C) \qquad (2)$$

where p is a constant, dependent upon prevailing mass transfer conditions, electrode area, solution volume, and cell geometry.[1] Combination of (1) and (2) yields

$$i = nFVp(C) \qquad (3)$$

The apparent number of faradays per mole of electroactive material, n_{app}, is determined experimentally and is defined as

$$n_{app} = \frac{\int_0^t i\,dt}{FV[(C_i) - (C)]} \qquad (4)$$

where (C_i) is the initial concentration of C. At the completion of electrolysis

$$n^0_{app} = \frac{\int_0^\infty i\,dt}{FV(C_i)} \qquad (5)$$

where the symbol n^0_{app} refers to evaluation of n_{app} at the completion of the electrolysis, where (C) approaches zero. Similar superscript notation is used below for (Z). Note that for case III, since all of substance Y is eventually electrolyzed, the denominators of (4) and (5) contain the additional terms $+FV[(Y_i) - (Y)]$ and $+FV(Y_i)$, respectively.

Case I.—The electroactive species C is consumed before and during electrolysis by a first- or pseudo-first-order reaction

$$C(+\ Z) \xrightarrow{k} X \qquad (6)$$
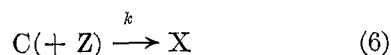
where Z is present in large excess, and $k' = k(Z)$. C and Z are mixed at time $t = 0$, and the electrolysis is started at $t = t_1$. The system is described by the equations

$$d(C)/dt = -k'(C) \quad 0 < t < t_1 \qquad (7)$$

$$d(C)/dt = -p(C) - k'(C) \quad t > t_1 \qquad (8)$$

At t_1, from (7) and the initial condition $(C) = (C_i)$ at $t = 0$

$$(C)_{t_1} = (C_i)\exp(-k't_1) \qquad (9)$$

where $(C)_{t_1}$ is the concentration of C at t_1. Solving (8), using (9) as a boundary condition

$$(C) = (C_i)\exp[-k't - p(t - t_1)] \qquad (10)$$

Combination of (3), (5), and (10) yields

$$n^0_{app} = npe^{pt_1}\int_{t_1}^\infty e^{-(p+k')t}\,dt \qquad (11)$$

and

$$n^0_{app}/n = \exp(-k't_1)/(1 + \gamma') \qquad (12)$$

where $\gamma' = k'/p$. Plotting $\log(n^0_{app}/n)$ vs. t_1, as shown in Fig. 1, allows the determination of k' and p from the slope and intercept of the line, respectively.
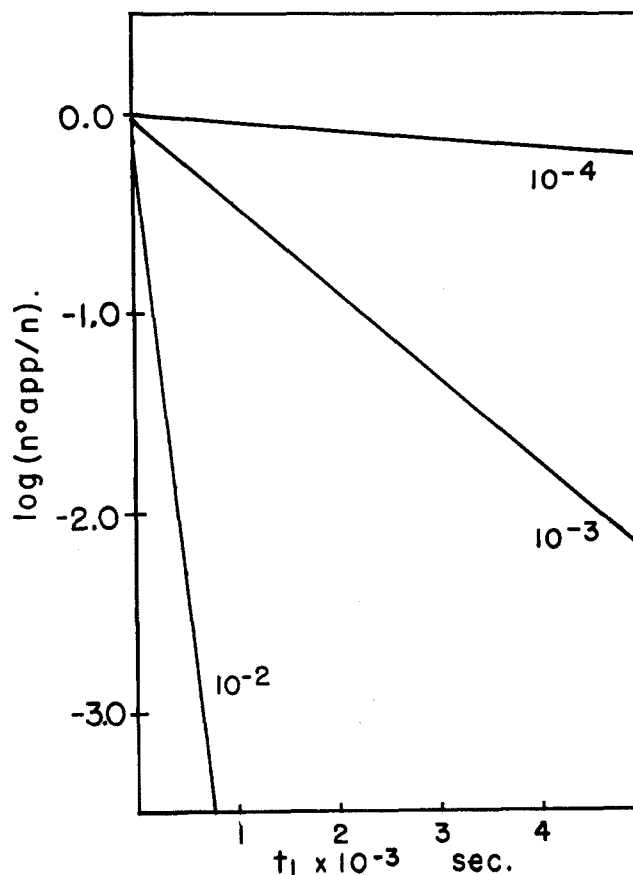

Fig. 1.—Case I: Variation of $\log n^0_{app}/n$ with t_1 for different values of k' shown on curves, calculated for $p = 0.03$ sec.$^{-1}$.

Case II.—The electroactive species C is consumed before and during the electrolysis by a second-order reaction.

$$(a) \qquad\qquad C + Z \xrightarrow{k} X$$

C and Z are mixed at $t = 0$, and the electrolysis is started at $t = t_1$. The system is described by the equations

$$d(C)/dt = -k(C)(Z) \quad 0 < t < t_1 \qquad (13)$$

$$d(C)/dt = -p(C) - k(C)(Z) \\ t > t_1 \qquad (14)$$

$$d(Z)/dt = -k(C)(Z) \qquad t > 0 \qquad (15)$$

At t_1, from (13), (15), and the initial conditions $(C) = (C_i)$ and $(Z) = (Z_i)$ at $t = 0$,[3]

$$(C)_{t_1} = \frac{(C_i)[(Z_i) - (C_i)]}{(Z_i)e^{[(Z_i)-(C_i)]kt_1} - (C_i)} \qquad (16)$$

$$(Z)_{t_1} = \frac{(Z_i)[(C_i) - (Z_i)]}{(C_i)e^{[(C_i)-(Z_i)]kt_1} - (Z_i)} \qquad (17)$$

Dividing (14) by (15) yields

$$d(C)/d(Z) = 1 + 1/[\gamma(Z)] \qquad (18)$$

where $\gamma = k/p$. Solution of (18) for (C), using the boundary condition $(C) = (C)_{t_1}$ and $(Z) = (Z)_{t_1}$ at $t = t_1$, yields, for $t > t_1$

$$(C) = (C)_{t_1} + (Z) - (Z)_{t_1} + \gamma^{-1}\ln[(Z)/(Z)_{t_1}] \qquad (19)$$

(3) See e.g. equivalent forms in A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York, N. Y., 1953, Chapter 2
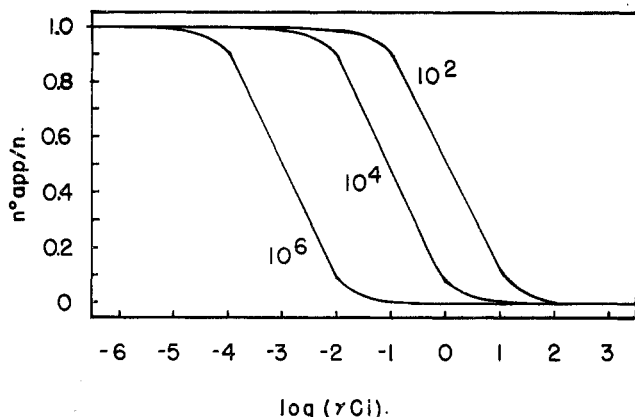
Fig. 2.—Case II(a): Variation of n^0_{app}/n with $\gamma(C_i)$ for different values of t_1 shown on curves, calculated for $(Z_i)/(C_i) = 1.0$.
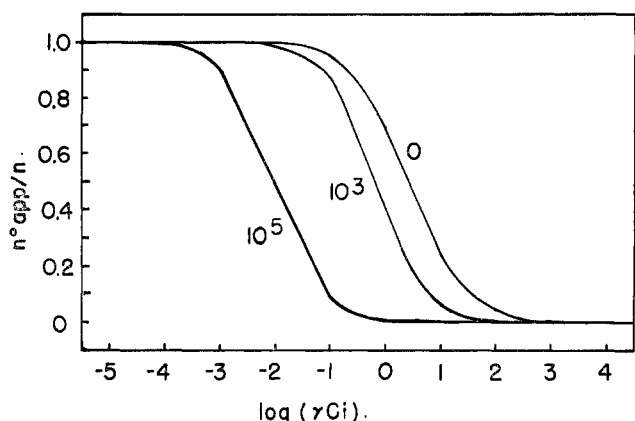

Fig. 3.—Case II(b): Variation of n^0_{app}/n with $\gamma(C_i)$ for different values of t_1 shown on curves.

From (3) and (15)

$$\int_{t_1}^{\infty} i \, dt = nFpV \int_{t_1}^{\infty} (C)dt =$$
$$\frac{nFV}{\gamma} \int_{(Z)^0}^{(Z)t_1} d(Z)/(Z) \quad (20)$$

Combining (5) and (20) yields

$$n^0_{app}/n = [\gamma(C_i)]^{-1} \ln [(Z)_{t_1}/(Z)^0] \quad (21)$$

An implicit relation for $(Z)^0$ is obtained from (19)

$$(Z)^0 = (Z)_{t_1} - (C)_{t_1} + \gamma^{-1} \ln [(Z)_{t_1}/(Z)^0] \quad (22)$$

An explicit relation for γ is obtained by combining (21) and (22)

$$\gamma = \frac{n}{n^0_{app}(C_i)} \ln \left[\frac{(Z)_{t_1}}{(Z)_{t_1} - (C)_{t_1} + n^0_{app}(C_i)/n} \right] \quad (23)$$

n^0_{app}/n can be evaluated by appropriate combination of (16), (17), and (23).

For the special case $(C_i) = (Z_i)$

$$(C)_{t_1} = (Z)_{t_1} = (C_i)/[1 + (C_i)kt_1] \quad (24)$$

and from (23) and (24)

$$\gamma = \frac{n}{n^0_{app}(C_i)} \ln \left[\frac{n/n^0_{app}}{1 + (C_i)kt_1} \right] \quad (25)$$

Variation of n^0_{app}/n with (C_i), (Z_i), γ, and t_1 is shown in Fig. 2 and Table I.

TABLE I

VARIATION OF n^0_{app}/n WITH $(Z_i)/(C_i)$, t_1, AND $\gamma(C_i)$

[n^0_{app}/n depends only upon the product $\gamma(C_i)$ at a given t_1]

t_1 (sec.)	n^0_{app}/n for $\gamma (C_i)$ of—			
	0.01	0.10	1.00	10.0
	$(Z_i)/(C_i) = 1.0$			
0	0.990	0.913	0.567	0.175
10	.990	.912	.564	.169
10^2	.989	.904	.533	.133
10^3	.980	.836	.352	.053
10^4	.901	.477	.084	.009
10^5	.498	.090	.010	.000
	$(Z_i)/(C_i) = 5.0$			
0	0.953	0.674	0.179	0.021
10	.952	.671	.171	.014
10^2	.948	.643	.115	.000
10^3	.907	.426	.003	.000
10^4	.592	.010	.000	.000
10^5	.014	.000	.000	.000
	$(Z_i)/(C_i) = 17.0$			
0	0.855	0.375	0.057	0.006
10	.854	.369	.048	.001
10^2	.841	.318	.011	.000
10^3	.723	.074	.000	.000
10^4	.166	.000	.000	.000

(b) $2C \xrightarrow{k} X$ (26)
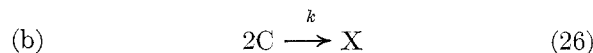
The solution is prepared at $t = 0$, and electrolysis is started at t_1. The system is described by the equations

$$d(C)/dt = -k(C)^2 \qquad 0 < t < t_1 \quad (27)$$
$$d(C)/dt = -k(C)^2 - p(C) \qquad t > t_1 \quad (28)$$

Up to t_1, $(C)_{t_1}$ is given by (24). An equation for (C) is obtained from (28) and (24)

$$(C) = (C_i)/\{ [\gamma(C_i) + 1 + (C_i)kt_1] e^{p(t-t_1)} - \gamma(C_i) \} \quad (29)$$

n^0_{app}/n is evaluated from (3), (5), and (29)

$$\frac{n^0_{app}}{n} = \frac{p}{(C_i)} \int_{(C)t_1}^{0} (C)dt = \frac{p}{(C_i)} \int_0^{(C)t_1} \frac{d(C)}{k(C) + p} \quad (30)$$

and, using (24)

$$\frac{n^0_{app}}{n} = \frac{1}{\gamma(C_i)} \ln \left[1 + \frac{\gamma(C_i)}{1 + (C_i)kt_1} \right] \quad (31)$$

Variation of n^0_{app}/n with $\gamma(C_i)$ and t_1 is shown in Fig. 3.

Case III.—The electroactive species C is formed by a reversible reaction

$$Y \underset{k_b}{\overset{k_f}{\rightleftarrows}} C \quad (32)$$

The system is described by the equations

$$d(C)/dt = -p(C) + k_f(Y) - k_b(C) \quad (33)$$
$$d(Y)/dt = -k_f(Y) + k_b(C) \quad (34)$$

Equations 33 and 34 are solved conveniently by using the LaPlace transform method, with the initial condition $(C) = (C_i)$ and $(Y) = (Y_i)$ at $t = 0$. The results are
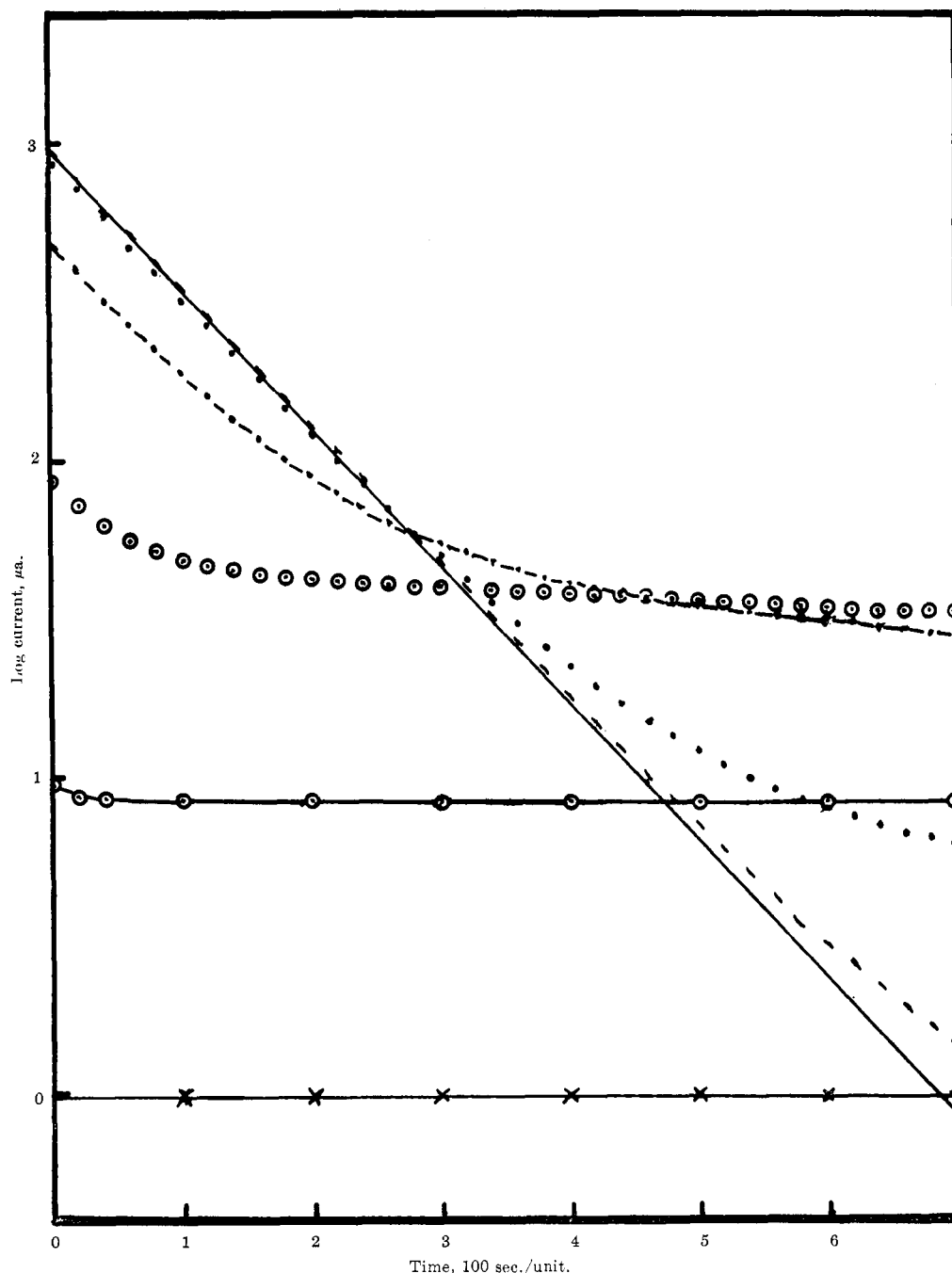
Fig. 4.—Case III: Log i vs. t for different values of $K = k_f/k_b$, calculated for $(C_i) + (Y_i) = 10^{-4} M$, $p = 0.01$ sec.$^{-1}$, and $k_f = 10^{-3}$ sec.$^{-1}$: $\times$——$\times$, $K = 0.001$; $\odot$——$\odot$, $K = 0.01$; $\odot$, $K = 0.1$; ——·——, $K = 1.0$; •°•, $K = 10.0$; ———, $K = 100.0$; ——, $K = \infty$.

$$(C_i)/(Y_i) = k_f/k_b = K \qquad (35)$$

$$(C) = (C_i)e^{-Lt}\left\{\cosh(Gt) + [(k_b + k_f - p)/2G]\sinh(Gt)\right\} \qquad (36)$$

where L and G are given by

$$L = 0.5(p + k_b + k_f) \qquad (37)$$

$$G = (L^2 - k_f p)^{1/2} \qquad (38)$$

Note that under all circumstances, since the total amount of electroactive species, $(Y_i) + (C_i)$, is eventually electrolyzed, $n^0_{app} = n$. The presence of a preceding chemical reaction will only affect the current–time behavior, causing curvature of log i vs. t plots, or variation of the "apparent-p" for the electrolysis. The current–time equation is obtained by combining

(3) and (36). Log i–t curves for several values of k_f and k_b are shown in Fig. 4 and 5.

Discussion

For those cases in which C is converted to a nonelectroactive species by a chemical reaction (cases I and II) n^0_{app} varies with t_1, k, p, (C_i), and (Z_i). When the concentration of Z is initially about twenty or more times the initial concentration of C, the reaction is essentially pseudo-first order, and can be treated as case I, with n^0_{app} being independent of the (C_i). Taking p as adjustable between 10^{-1} and 10^{-4} sec.$^{-1}$, and assuming usual values for the other variables, k' in the range of 10^{-1} to 10^{-5} sec.$^{-1}$ will lead to nonintegral values of n^0_{app}. In common with other coulometric determinations in which the current decays to background level, relatively little rate constant information
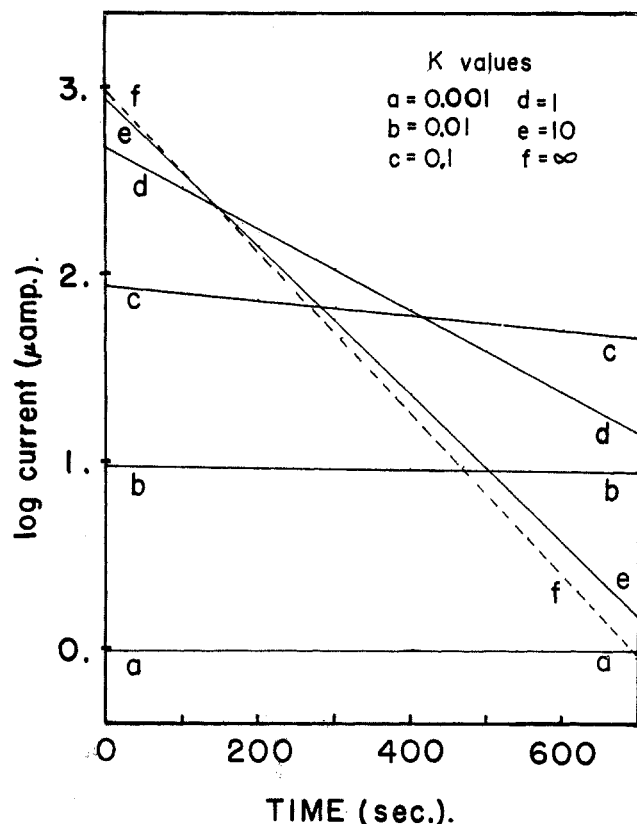
Fig. 5.—Case III: Log i vs. t for different values of $K = k_f/k_b$, calculated for $(C_i) + (Y_i) = 10^{-4}\ M$, $p = 0.01$ sec.$^{-1}$, and $k_f = 10$ sec.$^{-1}$

can be obtained from log i–t curves. For case III, generation of C by a preceding chemical reaction, on the other hand, rate constant data can only be obtained from log i–t curves, since in all cases $n^0_{app} = n$. Reactions of this type are indicated when integral, constant, n^0_{app} values are obtained under a variety of experimental conditions, and log i–t curves show appre-

ciable curvature, or have slopes which are smaller than usual. Both k_f and k_b determine the shape of the log i–t curves. When $k_f > 100\ k_b$, 99% of the total species is initially present in the electroactive forms, and the i–t behavior differs only very slightly from the uncomplicated behavior. When k_f/k_b is small, then the current may take a long time to decay to the background level, even for k_f values which are large compared to p (Fig. 5). In general, a preceding reaction with a K in the range of 100 to 0.01 can be investigated.

Reaction schemes corresponding to the preceding cases are probably fairly common in controlled potential coulometry. Cases I and II occur whenever the electroactive species can react with the solvent, supporting electrolyte, oxygen, etc. Analytical coulometric data can be corrected for the effect of side reactions by techniques suggested in these studies. The reaction of α,α-diphenylpicrylhydrazyl (DPPH) with bromide ion during the electroreduction of DPPH in an acetonitrile solution of tetrabutylammonium bromide was studied coulometrically by this technique.[4] Reactions of the type described in case III might have been responsible for the curvature in log i–t curves obtained during the coulometric determination of tin.[5] A recent communication on the coulometry of the uranium(VI)–uranium(IV) system in a tripolyphosphate medium indicated that the electrolysis time for the reoxidation of U(IV) was much longer than that for the reduction of U(VI).[6] This difference in electrolysis times under essentially identical cell conditions may be due to a slow chemical reaction step during the anodic oxidation.

(4) E. Solon and A. J. Bard, to be submitted for publication.
(5) A. J. Bard, *Anal. Chim. Acta*, **22**, 577 (1960).
(6) H. E. Zittel and L. B. Dunlap, *Anal. Chem.*, **35**, 125 (1963).

SALT EFFECTS ON THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID AND IONIZED α-NAPHTHOIC ACID AND ON THE DISSOCIATION CONSTANT OF α-NAPHTHOIC ACID IN 50 WEIGHT PER CENT DIOXANE–WATER[1a]

By ARTHUR F. BUTLER AND ERNEST GRUNWALD[1b]

Chemistry Department, Florida State University, Tallahassee, Florida

Received April 25, 1963

Activity coefficients are reported for millimolal hydrochloric and ionized α-naphthoic acid (H,Cl and H,A) in 50 wt. % dioxane–water in the presence of 0.04–0.6 m NaCl, NaClO$_4$, (CH$_3$)$_4$NCl, and sodium β-naphthalene-sulfonate (NaNs) at 25°. The observed salt effects indicate that salt-induced medium effects make only a relatively small contribution to $\gamma_{H\gamma Cl}$ and $\gamma_{H\gamma A}$ and are masked by other interactions. There are significant specific differences between the salt effects of NaCl and NaClO$_4$ on the one hand, and those of (CH$_3$)$_4$NCl and NaNs on the other, in such a direction as to suggest stabilizing interactions with the large organic ions. In particular, there is evidence for specific attractive interactions between the two naphthyl anions A$^-$ and Ns$^-$. The values of $\gamma_{H\gamma A}$ are based on measurements of the solubility[2] and acid dissociation constant of α-naphthoic acid in these salt solutions.

We wish to report a study of salt effects on the activity coefficients of hydrochloric acid ($\gamma_{H\gamma Cl}$) and

ionized α-naphthoic acid ($\gamma_{H\gamma A}$) and on the acid dissociation constant of α-naphthoic acid, in a solvent consisting of 50.00 wt. % dioxane–50.00 wt. % water at 25°. The dielectric constant of this solvent is 35.85.[3]

(1) (a) Work supported by Office of Naval Research; reproduction in whole or in part is permitted for any purpose of the United States government; (b) Bell Telephone Laboratories, Inc., Murry Hill, N. J.
(2) E. Grunwald and A. F. Butler, *J. Am. Chem. Soc.*, **82**, 5647 (1960).

(3) F. E. Critchfield, J. A. Gibson, and J. L. Hall, *ibid.*, **75**, 1991 (1953).