of some sort with the solvent. The application of equation (5) to these cases even at the wave lengths of maximum absorbancy requires that the correction for the absorbancy of uncomplexed halogen be nearly as great as the absorbancy of the solution itself. The points obtained in such calculations were widely scattered, and lines of negative slope were often encountered. In all cases the values of the equilibrium constant for complexing were near zero with a high standard deviation whether they were negative or positive. It is certain that trifluoroacetic acid does interact with the halogens as shown in the absorption spectra, but the extent of the interaction cannot be measured accurately by this method. The equilibrium constant in the case of iodine and iodine chloride with trifluoroacetic acid was of the order of 0 ± 0.9 where 0.9 sets the 95% confidence limits of the values.

Inconclusive results were obtained with bromine in both acetic and trifluoroacetic acids. In the former case especially, it was necessary to use

small differences of large absorbancy values in the calculations.

The highly polar trifluoroacetic acid (the dielectric constant is 42.1 at $25°$[14] even though largely in the relatively non-polar dimeric form[12]) and 96% sulfuric acid (the dielectric constant is greater than 84 at $20°$)[15] were evidently not nearly as effective in complexing with halogens as was the much less polar acetic acid (the dielectric constant is 6.13 at $20°$).[16] It seems reasonable to conclude that the very structural features which make trifluoroacetic acid and sulfuric acid such strong proton donors would make them exceedingly weak electron donors. Consequently such solvents would not be expected to complex with halogens as well as more basic substances (e.g., acetic acid) in spite of the fact that they are very polar in nature.

(14) J. H. Simons and K. E. Lorentzen. THIS JOURNAL, **72**, 1426 (1950).

(15) P. Walden, Z. physik. Chem., **46**, 182 (1903).

(16) C. P. Smyth and H. E. Rogers, THIS JOURNAL, **52**, 1824 (1930).

IOWA CITY, IOWA

Oscillographic Polarographic Waves for the Reversible Deposition of Metals on Solid Electrodes

BY TALIVALDIS BERZINS AND PAUL DELAHAY

An equation is derived for oscillographic polarographic waves corresponding to the reversible deposition of an insoluble substance. Theoretical results are compared with experimental data, and discrepancies are accounted for by variations of the activity of the deposit.

The following three major types of electrode processes should be considered in the development of the theory of oscillographic polarography: (1) electrode processes for which it can be assumed that electrochemical equilibrium is achieved between two soluble species; (2) reversible electrode processes yielding an insoluble substance; (3) irreversible electrode processes. The theoretical treatment of oscillographic waves corresponding to electrode processes of the first type was developed by Randles[1] and Sevcik.[2] The other two types of oscillographic waves were studied in this Laboratory, and the present paper deals with waves corresponding to the reversible deposition of an insoluble substance.

Equations for the Complete Wave and the Peak Current

Boundary and Initial Conditions.—Consider the reduction of a substance Ox to another substance Red which is insoluble in the solution containing substance Ox or in the electrode material. If electrochemical equilibrium is assumed to be achieved at the electrode, it is permissible to apply the Nernst equation in order to correlate the activities of the substances Ox and Red. In order to simplify the calculations it is convenient to con-

(1) J. E. B. Randles, Trans. Faraday Soc., **44**, 327 (1948).

(2) A. Sevcik, Collection Czechoslov. Chem. Communs., **13**, 349 (1948).

sider the case in which the activity of substance Red is assumed to be equal to unity. It can reasonably be expected that this hypothesis is verified when the electrode surface is coated with at least a monolayer of substance Red. When writing the Nernst equation it should be recalled that, in oscillographic polarography, the electrode potential E is a linear function of time of the form

$$E = E_i - vt \qquad (1)$$

In equation (1) E_i is the initial potential and v the rate of potential change. The second term $-vt$ on the right-hand of (1) is negative in the case of a cathodic process and positive for an anodic process, the European convention of electrode signs being used.

By taking equation (1) into account, the Nernst equation can be written under the form

$$(C_{ox})_{x=0} = \exp\left[\frac{nF}{RT}(E_i - E^0) - \ln f_{ox}\right]\exp\left[-\frac{nF}{RT}vt\right] \qquad (2)$$

where the subscript $x = 0$ indicates that C_{ox} is taken at the electrode surface; E^0 is the standard potential for the electrode process; f_{ox} the activity coefficient of the substance reacting at the electrode; and the other notations are conventional.

The initial potential E_i of the potential sweep should be such that virtually no current flows through the cell before the wave is recorded. Con-

sequently, the concentration of reacting substance at the electrode surface is essentially the bulk concentration C_0 of the reacting substance and the initial potential E_i should satisfy the relationship

$$E_i = E^0 + \frac{RT}{nF} \ln f_{ox} C_0 \tag{3}$$

The problem to be solved is to determine the concentration of the reducible substance as a function of the variables x and t. This is done by finding the solution of the differential equation expressing Fick's second law, for the boundary condition (2) and for the initial condition $C = C_0$ (for $t = 0$).

Equation of the Wave.—The present boundary value problem can be solved by applying Duhamels' theorem[3] or, more simply, by using the Laplace transformation.[4] By the latter method, one determines the transform of the solution by satisfying the boundary condition (2). The concentration C is then readily obtained by inverse transformation. The current density is derived by calculating the flux for $x = 0$, and by multiplying the result by the charge involved in the reduction of 1 mole of substance Ox. Thus

$$\left(\frac{\partial C}{\partial x}\right)_{x=0} = -C_0 i \left(\frac{\theta}{D}\right)^{1/2} \exp(-\theta t) \operatorname{erf}[i(\theta t)^{1/2}] \tag{4}$$

where θ is defined by

$$\theta = nFv/RT \tag{5}$$

In equation (4), $i = \sqrt{-1}$, and "erf" represents the error integral having the quantity between parentheses as upper limit. By noticing that[5]

$$\operatorname{erf}[i(\theta t)^{1/2}] = \frac{2i}{\pi^{1/2}} \int_0^{(\theta t)^{1/2}} \exp(z^2)\, dz \tag{6}$$

the imaginary i is dropped from (4). After introducing the value of θ from (5) one finally obtains

$$i = \frac{2}{\pi^{1/2}} \frac{n^{3/2}F^{3/2}}{R^{1/2}T^{1/2}} A C_0 D^{1/2} v^{1/2} \Phi\left[\left(\frac{nF}{RT} vt\right)^{1/2}\right] \tag{7}$$

where the notation $\Phi(\alpha)$ represents the function

$$\Phi(\alpha) = \exp(-\alpha^2) \int_0^\alpha \exp(z^2) dz \tag{8}$$

Values of this function were tabulated by Miller and Gordon.[6] By combining (1), (3) and (7), and introducing the numerical values of the various constants, one obtains the equation of the oscillographic wave for 25°

$$i = 679n^{3/2}A C_0 D^{1/2}v^{1/2}\Phi\left[6.25n^{1/2}\left(E^0 - E + \frac{0.0591}{n}\log f_{ox} C_0\right)^{1/2}\right] \tag{9}$$

where A is in cm.², C_0 in moles per liter, D in cm.² sec.$^{-1}$, v in volts sec.$^{-1}$, and i in amperes. From equations (7) and (9) it is seen that the current along the wave is proportional to the following factors: the area of the electrode, the concentration of reducible substance and the square root of the rate of potential change.

(3) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, London, 1947, p. 45.

(4) See for example R. V. Churchill, "Modern Operational Mathematics in Engineering," McGraw–Hill Book Co., Inc., New York, N. Y., 1944.

(5) Reference 3, p. 372.

(6) W. L. Miller and A. R. Gordon, J. Phys. Chem., 35, 2785 (1931).

Peak Current.—The function Φ defined by equation (8) exhibits a maximum equal to 0.5410 which corresponds to a value of 0.9241 of the argument.[6] On the basis of this value of Φ, one obtains the following equation for the peak current at 25°

$$i_p = 367n^{3/2}A C_0 D^{1/2}v^{1/2} \tag{10}$$

where the units are the same as in (9).

At the peak potential E_p, one has $\left(\frac{nF}{RT}vt\right)^{1/2} = $ 0.9241, or $vt = \frac{0.0218}{n}$ for 25°. Hence, on the basis of (1) and (3) one calculates for a temperature of 25°

$$E_p = E^0 + \frac{0.0591}{n}\log f_{ox} C_0 - \frac{0.0218}{n} \tag{11}$$

From (11) it is seen that the peak potential E_p depends on the bulk concentration of the substance being reduced at the electrode and that E_p is shifted toward more negative potentials as this concentration is decreased. Since C_0 is generally of the order of 10^{-3} mole per liter, or even smaller, calculated peak potentials are slightly more negative than the corresponding standard potentials.

In terms of the peak potential, the values of E for which equation (9) is applicable, should obey the following inequality which was obtained by combining equations (3) and (11)

$$E \leqslant E_p + \frac{0.0218}{n} \tag{12}$$

Case of Cylindric and Spherical Electrodes.—The present problem could be solved for the case of cylindric electrodes but the calculations are arduous. It is rather a simple matter to write the Laplace transform of the solution, but the derivation of the concentration from the transform is lengthy. The transform contains a combination of Bessel functions which does not lend itself to immediate inverse transformation. Therefore, it is necessary to apply the inversion theorem and this leads to cumbersome equations. Actually, the result would be hardly worth the labor since it was recently pointed out by Rius and co-workers[7] that problems of cylindric diffusion can be treated in terms of linear diffusion *under certain conditions*. The conclusion of these authors is based on the treatment of cylindric diffusion which will be found, for example, in the monograph of Carslaw and Jaeger.[8] From the equation reported by the latter authors, Rius, *et al.*, concluded that the current in the initial stage of an electrolysis at *constant potential* can be approximately calculated from the equation for linear diffusion. The error is smaller than 5% when the following condition is fulfilled

$$D\tau/r^2 \leqslant 3 \times 10^{-3} \tag{13}$$

where D is the diffusion coefficient of the substance reacting at the electrode, τ the time elapsed since the beginning of the electrolysis and r the radius of the electrode. By taking $D = 10^{-5}$ cm.² sec.$^{-1}$ and $r = 0.05$ cm., it is seen from (13) that the error does not exceed 5% when τ is smaller than 0.8 sec. The time corresponding to the ascending branch of a wave in oscillographic polarography is generally smaller than 1 or 2 sec., and consequently the above treatment of linear diffusion can be regarded as a first approximation for the corresponding problem in cylindric diffusion. A similar conclusion would also be reached for spherical electrodes. Another reason for not undertaking calculations for the cases of cylindric or spherical diffusion is that the present theory, at any rate, is approximate because of the assumption made in the writing of the boundary condition. More is said about this in the Experimental part.

(7) A. Rius, S. Polo and J. Llopis, *Anales Real Soc. Espan. Fís. y Quím.*, 45, 1029 (1949).

(8) See ref. 3, pp. 280–282.

Experimental

Linear Voltage Generator and Recording of Waves.—The oscillographic polarograph used in this study was essentially composed of a linear voltage generator and a cathode-ray oscillograph. The linear voltage was generated by charging a condenser connected in series with a large resistance. The voltage on the terminals of the condenser was applied to an amplifier having a low output resistance and the cell was fed by this amplifier. Details of the operation of the instrument, which is schematically shown in Fig. 1, are given below.
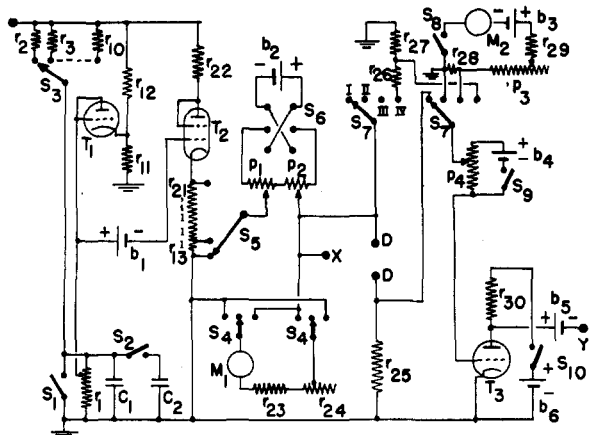

Fig. 1.—Schematic diagram of the linear voltage generator and related circuits (heater circuits not represented). The elements of the circuit are as follows. Resistances (2 watt resistors unless otherwise specified): r_1, 3.3 megohms adjustable; r_2, 2.2 megohms; r_3, 1.5 megohms; r_4, 1.0 megohm; r_5, 680 K.; r_6, 470 K.; r_7, 330 K.; r_8, 220 K., 4 watts; r_9, 150 K., 10 watts; 100 K., 10 watts; r_{11}, 25 K., adjustable; r_{12}, 100 K., 4 watts; r_{13} to r_{21}, 27 ohms; r_{22}, 10 K., 10 watts; r_{23}, 3.9 K.; r_{24}, 5 K. adjustable; r_{25}, 0 to 111, 111 ohms in 5 decades, 0.1% accuracy; r_{26}, 10 K., 0.1% accuracy; r_{27}, 0 to 100 ohms in 10 ohms steps, 0.1% accuracy; r_{28}, 10 ohms, 0.1% accuracy; r_{29}, 2 K.; r_{30}, 112 K. Potentiometers: p_1, 15 ohms; p_2, 100 ohms; p_3, 1 K.; p_4, 10 K. "Helipot" potentiometer, 10 turns. Condensers: C_1, 10 microfarads (oil); C_2, 20 microfarads (oil). Batteries: b_1, 15 volts, "C"; b_2, 4.5 volts, "A"; b_3, 1.5 volts, "A"; b_4, 3 volts, "A"; b_5, 45 volts, "B"; b_6, 90 volts, "B." Tubes: T_1, 6 J 5; T_2, 6 V 6; T_3, 6 F 5. Meters: M_1, 0-200 microamp.; M_2, 0-500 microamp.

By opening switch S_1, which is normally closed, condenser C_1 or $C_1 + C_2$ is allowed to charge through one of the resistances r_2 to r_{10}. The voltage on the terminals of C_1 or $C_1 + C_2$ is applied to tube T_2 whose cathode bias is an adjustable resistance r_{13} to r_{21}. A fraction of the voltage on the terminals of the cathode bias is applied to the polarographic cell connected in DD. The amplitude of the voltage sweep is limited by tube T_1 which becomes conductive when its plate potential reaches a certain positive value.[9] Resistance r_{11} is adjusted once and for all in such a manner that the total amplitude of the voltage sweep across r_{13} to r_{21} is of the order of 2 volts. The initial voltage applied to the cell is adjusted by means of potentiometers p_1 and p_2. The rate of potential change is varied by means of S_3 and by selecting the capacity of the condenser being charged (C_1 or $C_1 + C_2$). The ohmic drop across r_{25} is applièd, after amplification (T_3), to the "Y" input of a cathode-ray oscillograph (Du-Mont 304 H). The vertical deflection of this instrument is controlled by means of potentiometer p_4. Switch S_4 enables one to measure the initial voltage applied to the cell (meter M_1, calibrated in volts). The four positions of switch S_7 are as follows: I, recording of the oscillographic wave; II, zero voltage applied to the preamplifier; III, a 5-milli-

volt voltage is applied to the "Y" preamplifier (this voltage is the ohmic drop corresponding to a current of 0.0005 amp. in r_{28}); IV, recording of the voltage wave (voltage divider $r_{26} + r_{27}$). The "X" input of the oscillograph is connected to terminal X.

Electrolytic Cell.—Waves were recorded with a platinum cylindric electrode immersed in a 50-ml. polarographic cell of conventional design. The electrode was sealed at both ends in capillary tubes in order to reproduce as well as feasible the conditions of semi-infinite diffusion (see comments about the case of cylindric diffusion in the theoretical part). The exposed area of the electrode was 0.107 cm.[2]. The mercury pool in the cell was the anode of the electrolytic cell, and the potential of this electrode was kept at a constant value by using as supporting electrolyte a 1 molar potassium chloride solution saturated with mercurous chloride. The end of the platinum electrode was only a few millimeters from the surface of the anode in order to keep the resistance of the cell at a minimum. All determinations were made with 0.5 millimolar cadmium ion solutions. The solution in the cell was freed of oxygen in the usual manner by bubbling pure nitrogen through it for 30 minutes. Before each determination, the platinum electrode was cleaned in concentrated nitric acid and then thoroughly washed with distilled water. The temperature of the solution was 25 ± 0.1°.

The horizontal potential scale of the recording oscillograph was calibrated by applying a known voltage (measured with a Leeds and Northrup student potentiometer) to the polarographic cell and by recording the corresponding deflection on the screen of the oscillograph. Moreover, potentials were corrected for the ohmic drop in the circuit.

Description and Discussion of Results

Variations of the peak current (equation (10)) with the square root of the rate of potential change v are shown in Fig. 2 for the reduction of cadmium ion. The theoretical curve calculated on the basis of the diffusion coefficient $D = 0.72 \times 10^{-5}$ cm. sec.$^{-1}$ [10] at infinite dilution is also shown in Fig. 2.
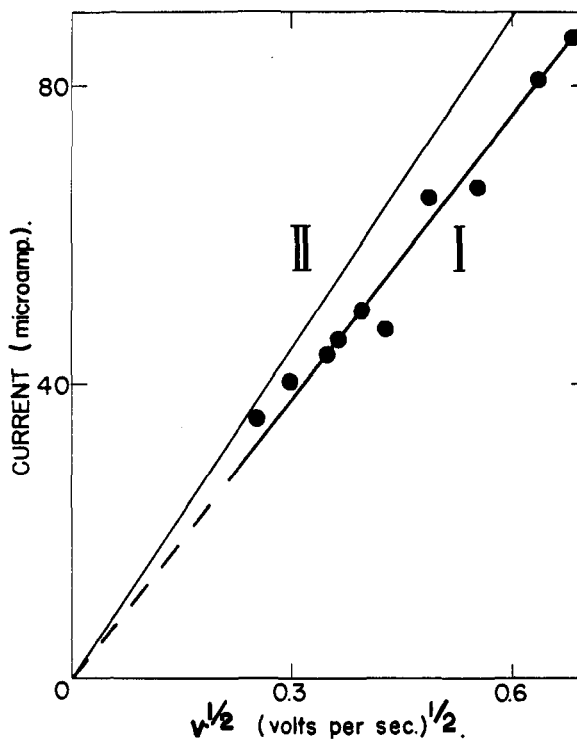

Fig. 2.—Variations of the peak current with the square root of the rate of potential change; deposition of cadmium on a platinum electrode: I, experimental line; II, calculated line. See data in text.

(9) See for example, F. C. Snowden and H. T. Page, *Anal. Chem.*, **22**, 969 (1950).

(10) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 45.

Notice that experimental currents are about 20% lower than the calculated values. This discrepancy partially results from the use of the value of D for infinite dilution, which is too high. Furthermore, there is some uncertainty about the term "A" in equation (10) because the effective area of a solid electrode may appreciably differ from the area one calculates from the dimensions of the electrode. By taking these various causes of discrepancy into account, one can conclude that there is a satisfactory agreement between experimental currents and the values calculated from (10). However, the reproducibility of results obtained under apparently identical conditions was poor. This matter is discussed below.

Experimental (I) and calculated (II) waves for the deposition of cadmium are compared in Fig. 3 (see equation (9)). In order to facilitate the comparison of curves I and II, it was assumed that the corresponding peak currents were identical (see Fig. 1 for discrepancies). Notice that the experimental wave is observed at less cathodic potentials than those one would expect from the present theory.[11] Furthermore, the ascending branch of the experimental wave is less steep than the corresponding segment of the theoretical wave. These discrepancies as well as the poor reproducibility indicated by Fig. 2 can be explained in the following manner.

TIME (SEC.).

CURRENT.   20 microamp.
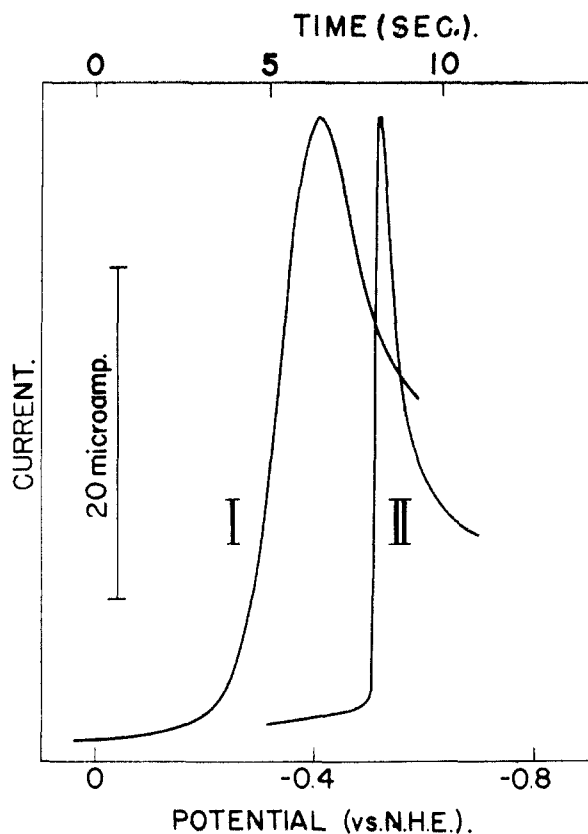
I   II

POTENTIAL (vs.N.H.E.).

Fig. 3.—Comparison of experimental (I) and theoretical (II) waves for the deposition of cadmium on platinum: rate of potential change, $v = 0.063$ volt sec.$^{-1}$; potentials in volts.

(11) The shift E_p toward anodic potentials was generally smaller than that in Fig. 2.

It was assumed in the theoretical treatment that the activity of the deposit is equal to unity. This is a simplifying hypothesis since, at the initial potential of the voltage sweep, virtually no metal is deposited on the electrode. Consequently the activity of the deposit at the initial potential of the wave is much smaller than unity. However, as soon as a low current has flowed through the cell, a sufficiently large number of atoms of metal has been produced to coat the electrode with at least a complete monolayer of deposit. Once this monolayer is formed, the activity of the deposit can be regarded as equal to unity and the theoretical treatment is valid. In the present case, for an electrode area of 0.107 cm.^{2} the deposition of a complete monolayer of cadmium requires 2.21 $\times$ 10^{-6} coulomb. From Fig. 3 it is seen that this quantity of electricity which corresponds to a current of 2.21 microamp. during 1 sec., had been supplied to the cell in the bottom segment of the wave. Thus, a monolayer of cadmium should have been formed at potentials corresponding to the lower segment of the wave, provided that the deposit of cadmium had been uniformly distributed. The obvious conclusion to be drawn from Fig. 3 is that the latter condition is not fulfilled and that deposition occurs at "active centers" on the electrode surface. As a result, the complete coating of the inert electrode by cadmium requires the deposition of a number of cadmium atoms corresponding to several monolayers. Since the electrode is coated progressively as the potential varies, there is a continuous variation of the activity of the deposit along the wave. As a result, the boundary condition expressed by equation (2) should be modified in order to take into account the variation of the activity of the deposit with time. Unfortunately, such a relationship is not known or cannot be postulated and a more refined treatment is not possible.

It was observed that the peak potential was shifted toward the theoretical value as the rate of potential was increased. For example, the peak potential E_p was equal to -0.401 volt (vs. N.H.E.) for $v = 0.060$ volt sec.$^{-1}$, whereas E_p was equal to -0.482 volt for $v = 0.207$ volt sec.$^{-1}$. The theoretical value of E_p as calculated from (11) was -0.510 volt (N.H.E.).[12] Thus, the distribution of cadmium atoms at the surface of the inert electrode became more uniform as the duration of electrolysis was decreased. This shift of the peak potential with the rate of potential change is even more significant if one considers that the number of atoms deposited during the recording of a wave decreases as the rate of potential change is increased (i_p is proportional to $v^{1/2}$).

Summarizing, the present study shows that oscillographic waves corresponding to the deposition of an insoluble material onto a solid electrode are strongly affected by variations of the activity of the deposit. Because the properties of the

(12) There is some uncertainty about the theoretical value of E_p because the activity coefficient of cadmium ion is not known exactly on account of complexation with chloride ion. In the calculation leading to the value $E_p = -0.510$ volt this coefficient was assumed to be equal to unity, but actually f_{ox} is smaller than unity and the resulting value of E_p is somewhat more cathodic than -0.510 volt.

electrode surface vary from one experiment to another, fluctuations in the peak current are observed and consequently the method is not to be recommended for analytical applications. On the other hand, the present method offers the possibility of studying indirectly the factors which might affect the uniformity of an electrolytic deposit having, say, ten atomic radii.

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BATON ROUGE, LOUISIANA

The Effect of Solvent on Equilibrium and Rate Constants. II. The Measurement and Correlation of Acid Dissociation Constants of Anilinium and Ammonium Salts in the System Ethanol–Water[1,2a]

BY BORIS GUTBEZAHL[2b] AND ERNEST GRUNWALD

An extrathermodynamic relationship, the activity postulate, has been valuable in predicting the solvent dependence of equilibrium and rate constants in hydroxylic solvents. It is now tested further by means of the acid dissociation constants of anilinium and ammonium salts in the system ethanol–water. The acid dissociation constants of anilinium, p-toluidinium and N-methylanilinium chlorides are measured at 25.0 ° in ethanol–water mixtures containing 0, 20, 35, 50, 65, 80 and 95% wt.% ethanol. Published ratios of dissociation constants are recalculated on the basis of the new data to give acid dissociation constants, accurate to 0.05 pK unit, for eleven ammonium and anilinium salts. The solvent dependence of the acid dissociation constants is described quantitatively—as required by the activity postulate—by means of an activity function Y_0 and a set of parameters m_{BH} characteristic of the ammonium or anilinium salts. Values of Y_0 and relative values of m_{BH} are tabulated. The reaction constant ρ in the Hammett equation for the acid dissociation constants of m- and p-substituted anilines is solvent dependent, and a linear relationship between ρ and Y_0 is predicted and observed. In polar hydroxylic solvents, the substituent constant σ for polar substituents is also solvent dependent whenever the electron distribution is affected by solvation of the polar substituent. Criteria are given for detecting this effect. The general conditions for the existence of acidity functions are developed, and it is shown that the acidity functions H_0 and H_- do not exist in the system ethanol–water.

Many equilibria in solution are of the type

$$BZ + CZ' = BZ' + CZ \qquad (1)$$
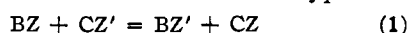
where B and C are organic radicals, and Z and Z' are functional groups. The mathematical analysis of the effect of a change in structure or solvent on this equilibrium involves four independent variables, corresponding to B, Z, Z' and the solvent; the variable corresponding to C is not independent, for the equilibrium constant is unity when B = C.

The analysis is often carried out with so-called degenerate activity coefficients.[1] The equilibrium constant at infinite dilution, K, is written as

$$K = K^w \frac{f_{BZ} f_{CZ'}}{f_{BZ'} f_{CZ}} \qquad (2)$$

where K^w is the equilibrium constant in water at infinite dilution, and the f's are the degenerate activity coefficients in the infinitely dilute non-aqueous solution referred to the infinitely dilute aqueous state. The formulation (2) is advantageous for the study of equilibria, particularly in hydroxylic solvents. In the special case where Z and Z' are constant, *i.e.*, where the analysis is limited to just one type of equilibrium, the solvent dependence of the ratios $f_{BZ}/f_{BZ'}$ is often simple and predictable. For example, we have noted on two previous occasions[1,3,4] that values of $\log f_{BZ}/f_{BZ'}$ for any two radicals B_1 and B_2 of the same electrical

character remained proportional as the hydroxylic solvent is varied. These observations have led us to propose the *activity postulate*

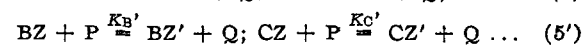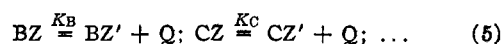$$\log f_{BZ}/f_{BZ'} = m_B Y_{Z,Z'} \qquad (3)$$

where the quantity m_B is independent of solvent and characteristic of B; and where $Y_{Z,Z'}$—the *activity function* for the two functional groups Z and Z'—depends only on the solvent.[1,3] The activity postulate thus separates $\log f_{BZ}/f_{BZ'}$ into two factors, m_B and $Y_{Z,Z'}$, which each depend on just one variable—a great simplification of the functional relationships.

According to equations (2) and (3), the dependence on solvent and structure of equilibrium constants for reactions like (1) is given by

$$\log K - \log K^w = \log f_{BZ}/f_{BZ'} - \log f_{CZ}/f_{CZ'} =$$
$$(m_B - m_C)Y_{Z,Z'} \qquad (4)$$

which implies the existence of linear free energy relationships.[5]

The use of the degenerate activity coefficients is also advantageous in the analysis of equilibria like (5) and (5').

$$BZ \overset{K_B}{=} BZ' + Q; \; CZ \overset{K_C}{=} CZ' + Q; \; \dots \qquad (5)$$

$$BZ + P \overset{K_B'}{=} BZ' + Q; \; CZ + P \overset{K_C'}{=} CZ' + Q \dots \qquad (5')$$

Equations analogous to (2) giving K_B, K_C, $\dots$, as functions of degenerate activity coefficients contain the ratios $f_{BZ}/f_{BZ'}$ to which the activity postulate (3) may apply, especially in hydroxylic solvents. In particular, if only *relative* equilibrium constants $K_R = K_B/K_C$ or K_B'/K_C' are of interest, equation (2) applies directly with $K = K_R$, and

(1) Part I of this series: E. Grunwald and B. J. Berkowitz, THIS JOURNAL, **73**, 4939 (1951).

(2) (a) This work has been supported by a grant-in-aid from the Research Corporation; (b) Atomic Energy Commission Predoctoral Fellow at Florida State University, 1951–1952. This article is based on the Ph.D. Dissertation of Boris Gutbezahl, deposited in the Library of Florida State University, Tallahassee, Fla., 1952.

(3) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948).

(4) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., 1940, New York, N. Y., chap. VII.