

Derivation and application of the linearized current-potential characteristic

David M. Mohilner, Norman. Hackerman, and Allen J. Bard

Anal. Chem., 1967, 39 (12), 1499-1501 • DOI: 10.1021/ac60256a016 • Publication Date (Web): 01 May 2002

Downloaded from <http://pubs.acs.org> on February 19, 2009

More About This Article

The permalink <http://dx.doi.org/10.1021/ac60256a016> provides access to:

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article



DISCUSSION

It is confirmed above that the migrations of ions on Amberlite SA-2 ion-exchange paper in aqueous-organic wash liquids can usually be predicted from batch equilibrium and column studies with the same solvent and a comparable resin. Likewise, rapid migrations on these ion-exchange papers can often be used to pre-evaluate wash liquids for column ion-exchange separations. There are discrepancies present, however, which indicate that results in the two media are not necessarily identical. These discrepancies may be due to the differences in the techniques of column and paper chromatography (5) which can lead to certain effects in the latter which can be accounted for and possibly eliminated, such as frontal separation of the wash liquid in several of the systems mentioned above. Or, they may be due to basic differences in the nature of the stationary phases (6) of the chromatographic systems involved, which can lead to unexplainable anomalous results such as for bismuth on SA-2 paper.

Results on MN ion-exchange papers are quite similar to those on Whatman No. 1 cellulose paper with mixed wash liquids, as might be expected from the very low exchange capacity of these papers. Unlike Amberlite papers, MN papers do not generally yield the same information as batch equilibration or column experiments. This study does not

support the claim (8) that these papers "are superior to those which contain interspersed ion exchange resin." In addition, the rate of solvent flow is much slower on the MN papers than on Amberlite papers.

Three previous comparisons of Amberlite and MN papers for metal-ion migrations in aqueous-acid wash liquids showed that as in the present study, sorption on the MN papers was always lower than on the corresponding Amberlite paper (9-11).

Only the major separations which were predicted from individual migrations were tested and reported above. Many additional separations of pairs and triplets of ions can be planned and carried out, based on the R_F values presented in the tables. By selective qualitative tests, it should be possible to identify members of a group not completely separated from each other in a particular system.

RECEIVED for review April 21, 1967. Accepted August 3, 1967.

(8) MN Guide, Machery-Nagel and Co., Düren, West Germany, May 1965, p. 29.

(9) M. Lederer and F. Saracino, *J. Chromatog.*, **15**, 80 (1964).

(10) G. Bagliano and L. Ossicini, *J. Chromatog.*, **21**, 499 (1966).

(11) G. Bagliano, L. Ossicini, and M. Lederer, *J. Chromatog.*, **21**, 471 (1966).

CORRESPONDENCE

On Derivation and Application of the Linearized Current-Potential Characteristic

SIR: Birke and Roe (1) discussed recently the derivation and accuracy of the well-known linearized current-potential characteristic (2) for electrode reactions controlled by charge transfer and mass transfer with particular reference to its applicability to the single pulse galvanostatic technique. Because the derivation given by these authors might give the impression that linearization of the complete expression

$$I(C_0, C_R, \eta) = I_{a^0} \left\{ \frac{C_0}{C_0^0} \exp(-\alpha\phi\eta) - \frac{C_R}{C_R^0} \exp[(1-\alpha)\phi\eta] \right\} \quad (1)$$

to yield

$$I = I_{a^0} \left(\frac{C_0}{C_0^0} - \frac{C_R}{C_R^0} - \phi\eta \right) \quad (2)$$

requires the following restrictive conditions:

(1) R. L. Birke and D. K. Roe, *ANAL. CHEM.*, **37**, 450 (1965).

(2) P. Delahay, "Advances in Electrochemistry and Electrochemical Engineering," Vol. 1, Chap. 5, Interscience, New York, 1961.

$$\alpha = \frac{1}{2} \quad (3)$$

and

$$\frac{C_0}{C_0^0} + \frac{C_R}{C_R^0} = 2 \quad (4)$$

(or another pair of complimentary restrictive conditions), we thought it worthwhile to reexamine the derivation of the linearized characteristic.

A complete Taylor expansion of $I(C_0, C_R, \eta)$, considering I as a function of three independent variables, C_0 , C_R , and η , rather than as a function of η alone, is given in the Appendix. The result is:

$$\frac{I}{I_{a^0}} = \sum_{j=1}^{\infty} \frac{1}{j!} \left\{ j \left(\frac{C_0}{C_0^0} - 1 \right) (-\alpha\phi\eta)^{j-1} - j \left(\frac{C_R}{C_R^0} - 1 \right) [(1-\alpha)\phi\eta]^{j-1} + (\phi\eta)^j [(-\alpha)^j - (1-\alpha)^j] \right\} \quad (5)$$

When only the linear ($j = 1$) terms are kept, Equation 2 results, without further restriction. When the square or para-

bolic ($j = 2$) terms are kept, the following equation results:

$$\frac{I}{I_a^0} = \frac{C_0}{C_0^0} [1 - \alpha\phi\eta] - \frac{C_R}{C_R^0} [1 + (1 - \alpha)\phi\eta] + \frac{(2\alpha - 1)}{2} (\phi\eta)^2 \quad (6)$$

This equation is identical to Equation 4 in (1), except that the additional term $\frac{(2\alpha - 1)}{2} (\phi\eta)^2$ is included. The form of the expansion, Equation 5, indicates that the linear form holds whenever $\phi\eta \ll 1$. Although it is true that the accuracy of the linear characteristic depends upon the values of C_0/C_0^0 and C_R/C_R^0 in a given experiment, and that the conditions implied by Equation 3 and Equation 4 will transform the parabolic Equation 6 into the linear one, they are not necessary in the derivation of the linear characteristic.

For the particular case of the galvanostatic experiment,

$$\frac{C_0}{C_0^0} - 1 = - \left(\frac{t}{\tau_c} \right)^{1/2} \quad (7)$$

$$\frac{C_R}{C_R^0} - 1 = \left(\frac{t}{\tau_a} \right)^{1/2} \quad (8)$$

where τ_c and τ_a are the cathodic and anodic transition times. Introduction of Equation 7 and Equation 8 into Equation 5 (or alternately, expansion of Equation 1 in terms of $t^{1/2}$ and η) yields:

$$\frac{I}{I_a^0} = \sum_{j=1}^{\infty} \frac{1}{j!} \left\{ -jt^{1/2}(\phi\eta)^{j-1} \left[\frac{(-\alpha)^{j-1}}{\tau_c^{1/2}} + \frac{(1-\alpha)^{j-1}}{\tau_a^{1/2}} \right] + (\phi\eta)^j [(-\alpha)^j - (1-\alpha)^j] \right\} \quad (9)$$

The error in using the linear form at small values of $\phi\eta$ can be taken as the ratio of the second-order terms (assuming the higher-order terms are negligible) to the linear terms. Two cases will be examined. When both species are soluble and $D_0^{1/2} C_0^0 = D_R^{1/2} C_R^0$, $(t/\tau_c)^{1/2} = (t/\tau_a)^{1/2} = x$, the ratio becomes:

$$- \frac{(\phi\eta + (\phi\eta)^2/2x)(2\alpha - 1)}{2 + \phi\eta/x}$$

For small values of $\phi\eta$, the second term in the numerator is small, and the error is of the order of $\phi\eta(2\alpha - 1)/2$. Since ϕ at 25°C is 0.039n mv⁻¹, the maximum error for a one-electron reaction ($\alpha = 0$ or 1) with $\eta = 1$ mv is about 2%.

When one form, for example the reduced form, is a solid, so that τ_a can be considered infinite, the ratio, with $(t/\tau_c)^{1/2} = x$, is

$$- \frac{\alpha\phi\eta - (\phi\eta)^2(2\alpha - 1)/2x}{1 + \phi\eta/x}$$

For this case, the error is of the order of $\alpha\phi\eta$.

In general, for estimation of the errors involved in using the linearized approximation Equation 2 in place of Equation 1, one may estimate the upper bound of the remainders after the first terms in each of the four infinite series contained in Equation 5. Each of these series may be shown to be absolutely convergent by the ratio test. The error in the current is defined as:

$$I_{\text{error}} = I - I_{LA}$$

where I is the current given by Equation 1 and I_{LA} is the current given by the linear approximation, Equation 2. Then it follows (3) that:

$$|I_{\text{error}}| \leq I_a^0 \left(\left| \frac{C_0}{C_0^0} - 1 \right| + \left| \frac{C_R}{C_R^0} - 1 \right| + 2 \phi\eta \right) \left(\frac{|\phi\eta|}{1 - |\phi\eta|} \right) \quad (10)$$

This error is clearly time dependent. For example, in the case of a potentiostatic experiment, one obtains by substituting the solution of the boundary value problem for C_0 and C_R (Equation 2) the following estimate of the error:

$$|I_{\text{error}}| \leq I_a^0 \left\{ \frac{A}{\lambda} [1 - e^{\lambda^2 t} \text{erfc}(\lambda t^{1/2})] \left(\frac{1}{C_0^0} - \frac{\kappa^{1/2}}{C_R^0} \right) + 2|\phi\eta| \right\} \left(\frac{|\phi\eta|}{1 - |\phi\eta|} \right) \quad (11)$$

where

$$A = D_0^{1/2} C_0^0 \lambda_0 - D_R^{1/2} C_R^0 \lambda_R$$

$$\lambda_0 = [I_a^0 \exp(-\alpha\phi\eta)] / nFD_0 C_0^0$$

$$\lambda_R = \{I_a^0 \exp[(1 - \alpha)\phi\eta]\} / nFD_R C_R^0$$

$$\kappa = D_R/D_0$$

$$\lambda = \lambda_0 D_0^{1/2} + \lambda_R D_R^{1/2}$$

Alternate approaches to the derivation of linearized forms of Equation 1 involve differentiation of Equation 1 and consideration of the limits of the differentials as η approaches zero (4) and expansion of Equation 1 in a power series using Lagrange's theorem (5). In general, the linear Equation 2 holds for sufficiently small values of η , regardless of the sum of C_0/C_0^0 and C_R/C_R^0 , condition 4, or the value of α .

APPENDIX

For a function $f(x, y, z)$ expanded around the point x_0, y_0, z_0 , Taylor's expansion is (3)

$$f(x, y, z) = f(x_0, y_0, z_0) + \sum_{j=1}^{\infty} \frac{1}{j!} \left(\delta_x \frac{\partial}{\partial x} + \delta_y \frac{\partial}{\partial y} + \delta_z \frac{\partial}{\partial z} \right)^j f(x, y, z) \Big|_{\substack{x = x_0 \\ y = y_0 \\ z = z_0}} \quad (A1)$$

where $\delta x = x - x_0$, $\delta y = y - y_0$, $\delta z = z - z_0$, and the expression in parenthesis is a differential operator raised to the j th power by formal application of the binomial theorem; the various powers of $\partial/\partial x$, $\partial/\partial y$, and $\partial/\partial z$ are regarded as symbols for repeated differentiation. After operation by the operator on the function $f(x, y, z)$, the limits are then taken at the point (x_0, y_0, z_0) .

For expansion of the particular function of interest, $I(C_0, C_R, \eta)$ (assuming α is constant), Equation 1, around the point corresponding to the equilibrium potential $I(C_0^0, C_R^0, 0)$

(3) C. R. Wylie, "Advanced Engineering Mathematics," pp. 602-4, McGraw-Hill, New York, 1951.

(4) K. Vetter, "Elektrochemische Kinetik," p. 265, Springer, Berlin, 1961.

(5) P. J. Gellings, *Z. Elektrochem.*, **66**, 477 (1962).

$$I = \sum_{j=1}^{\infty} \frac{1}{j!} \left(\delta C_o \frac{\partial}{\partial C_o} + \delta C_R \frac{\partial}{\partial C_R} + \delta \eta \frac{\partial}{\partial \eta} \right)^j \times I(C_o, C_R, \eta) \Big|_{(C_o^o, C_R^o, 0)} \quad (\text{A2})$$

where $I(C_o^o, C_R^o, 0) = 0$, $\delta C_o = C_o - C_o^o$, $\delta C_R = C_R - C_R^o$, $\delta \eta = \eta - 0 = \eta$, and $\phi = nF/RT$. Because of the form of Equation 1, derivatives involving $(\partial/\partial C_o)$ and $(\partial/\partial C_R)$ to powers higher than one, and $(\partial/\partial C_o)(\partial/\partial C_R)$, are zero, and (A2) may be written:

$$I = \sum_{j=1}^{\infty} \frac{1}{j!} \left\{ j \delta C_o \delta \eta^{j-1} \frac{\partial}{\partial C_o} \frac{\partial^{j-1}}{\partial \eta^{j-1}} + j \delta C_R \delta \eta^{j-1} \frac{\partial}{\partial C_R} \frac{\partial^{j-1}}{\partial \eta^{j-1}} + \delta \eta^j \frac{\partial^j}{\partial \eta^j} \right\} I(C_o, C_R, \eta) \Big|_{(C_o^o, C_R^o, 0)} \quad (\text{A3})$$

Substitution of the required derivatives and values for δC_o , δC_R , and $\delta \eta$ into Equation A3 yields Equation 5.

DAVID M. MOHILNER¹
NORMAN HACKERMAN
ALLEN J. BARD

Department of Chemistry
The University of Texas
Austin, Texas 78712

RECEIVED for review May 24, 1965. Resubmitted September 29, 1966. Accepted December 29, 1966. Work supported by the Robert A. Welch Foundation.

¹ Present Address, Department of Chemistry, Colorado State University, Fort Collins, Colorado.

Some Approximations for the Electrochemical Rate Equation and Their Applications

SIR: In a recent publication (1), we pointed out several aspects of the linearization of the following equation when it is applied to simple charge transfer processes in electrochemistry:

$$I(C_o, C_R, \eta) = I_a^o \left\{ \frac{C_o}{C_o^o} \exp(-\alpha\phi\eta) - \frac{C_R}{C_R^o} \exp[(1-\alpha)\phi\eta] \right\} \quad (1)$$

The external cell current density $I(C_o, C_R, \eta)$ is indicated to be a function of the surface concentrations of the oxidized C_o and reduced C_R forms of the species engaged in transfer of charge and of the overpotential η . The rate constant describing the process is embodied in the term I_a^o , the apparent exchange current density, the transfer coefficient is α and ϕ is nF/RT . The purpose of our previous discussion was restricted to the specific case of galvanostatic measurements where C_R/C_R^o was constant—e.g., $\text{Hg}_2^{+2} + 2e^- = 2\text{Hg}(l)$. Under such conditions, the linearized form of Equation 1, after substitution for the time dependence of C_o/C_o^o , was found not to hold to the same accuracy for a given η and α as when C_R was also time dependent. These points developed from the observation that experimental $\eta - t^{1/2}$ plots from galvanostatic measurements at the mercury electrode were not as straight as expected from the simple linear equation and inclusion of additional terms improved the agreement.

Subsequently there has been published a communication (2) which stresses that a derivation of the linearized expression can be obtained with the use of only the one restrictive condition that $\phi\eta \ll 1$. It was also stated that our use of other conditions to justify the applicability of the linearized approximation is unnecessary. We feel that the original conclusions can be reinforced by a careful comparison of the mathematical operations, including an examination of their physical significance. It will therefore be apparent that the approach of

Mohilner, Hackerman, and Bard (2) leads to the same result which we described. In addition, further aspects of galvanostatic $i - \eta - t^{1/2}$ curves will be given to illustrate the third dimension of the problem with particular reference to experimental conditions. It must be borne in mind that the following equations apply to simple charge transfer process and do not include charging of the electrode double layer.

Equation 1 of itself is not sufficient to describe an experimental measurement by controlled current or controlled potential methods unless it can be demonstrated that the concentration terms change a negligible amount during the departure from equilibrium. Depending upon the experiment, additional relations must be supplied which provide information about mass transport. For a controlled current experiment these relations are in general,

$$\frac{C_o}{C_o^o} = f(I', t); \quad \frac{C_R}{C_R^o} = g(I', t) \quad (2)$$

and for a controlled potential condition

$$\frac{C_o}{C_o^o} = h(\eta', t); \quad \frac{C_R}{C_R^o} = k(\eta', t) \quad (3)$$

where I' and η' represent time independent—i.e., amplitude parameters—and t may be expressed in terms of frequency in some cases. In Equations 2 and 3, the terms C_o/C_o^o and C_R/C_R^o are of the type of so-called intermediate variables because substitution of their functional forms in Equation 1 or a suitable approximation of Equation 1 always reduces by one the number of variables. Thus, contrary to statements by Mohilner *et al.* (2) there are *not* three independent variables in Equation 1 as applied to any of the types of measurements described. This conclusion clarifies the similarity of the two series approximations (1, 2) which are to be compared.

(1) R. L. Birke and D. K. Roe, *ANAL. CHEM.*, **37**, 450 (1965).

(2) D. M. Mohilner, N. Hackerman, and A. J. Bard, *ANAL. CHEM.*, **39**, 1499 (1967).