DISCUSSION

of the Lane-O'Dea-Osteryoung paper,
Statistical Properties of a Procedure
for Analyzing Pulse Voltammetric Data

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To supplement Lane's discussion of a statistical procedure for analyzing pulse voltammetric data, I would like to describe the experiment more fully in the context of the scientific problem being addressed. In a controlled-potential (voltammetric) experiment the current response generally depends on both potential and time. Since the current is the rate of charge transfer, the results of such experiments can be analyzed to yield the values of parameters that characterize the charge transfer process. The current for many charge transfer mechanisms can be calculated, although often the results (a current-potential curve, or voltammogram) can be obtained only numerically. The calculated voltammogram must be inverted to yield the values of the charge transfer parameters. It was the objective of O'Dea, et al. [1][1] to devise a procedure for this inversion that would not depend on either the charge-transfer mechanism or the choice of voltammetric experiment. However the specific problem addressed was that of determining the charge transfer parameters for the reduction of Zn(II) at mercury electrodes in aqueous solutions of $NaNO_3$.

It was assumed at the outset that the mechanism of charge transfer was described by the Butler-Volmer equation

$$i(t) = nFAk\epsilon^{-\alpha}[D_O^{1/2}C_O(O,t) - \epsilon D_R^{1/2}C_R(O,t)]$$

where $i(t)$ is the current at time t, n the number of electrons per zinc ion reduced, F the value of the Faraday, A the electrode area, D_O and D_R the diffusion coefficients of the oxidized (O) and reduced (R) forms of zinc. $C_O(O,t)$ and $C_R(O,t)$ are the corresponding concentrations at the electrode surface at time t,

$$\epsilon = \exp[(nF/RT)(E(t) - E_{1/2})]$$

where R is the gas constant, T the absolute temperature, E(t) is the imposed potential, which is a function of time, and k, α, and $E_{1/2}$ are the kinetic parameters as given by

Lane. A mathematical model which describes exactly the current-potential relation is developed by formulating the diffusion problem with the Butler-Volmer relation as a boundary condition and expressing the surface concentrations in terms of convolution integrals of currents to yield an integral equation for the current which can be solved numerically.

The typical procedure used in electrochemical kinetic studies is to measure $E_{1/2}$ independently and to use its value as a known quantity in analysis of the voltammogram. Furthermore, usually D_O, D_R, A, and n are determined in order to compare calculated and experimental currents directly. These additional pieces of information are not necessary, however, and may introduce systematic error into the values of the derived kinetic parameters. Because of the exponential form of the current-potential relation, minor errors in the value of $E_{1/2}$ distort the shape of the response and therefore cause errors in the derived value of α. These errors can even suggest a potential-dependence of α which is an artifact. In a differential experiment such as square wave voltammetry the response is generally peak-shaped, and the height of the peak reflects the values of k and α. Errors of normalization (e.g., measurement of A) therefore also introduce error into the values of the derived parameters.

From the discussion of Lane et al., it is clear that the normalization factor, a, is an unnecessary "nuisance" parameter, and thus it is foolish to confound the results of kinetic measurements by employing a method of data analysis which requires that a be known. The question of $E_{1/2}$ is more subtle, for experimental and chemical factors must be considered. In principle, knowing the true value of $E_{1/2}$ simplifies the problem. Potential differences can be measured accurately, but it is difficult to maintain a laboratory reference potential at a known value over time. The data of [1] and the data employed by Lane et al. display confidence intervals for $E_{1/2}$ at the 95% level of $\leqslant 0.001$ V. Working laboratory standards are not maintained with that precision. Chemical factors

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[1] Number in bracket is literature reference.

must also be considered. The value of $E_{1/2}$ is measured using either a voltammetric experiment with a much longer time scale or an equilibrium experiment. In the latter case the diffusion coefficients must also be known to yield $E_{1/2}$. In either case the change in time scale introduces the possibility of a change in mechanism, which produces a value of $E_{1/2}$ inappropriate for the conditions of the kinetic experiment. Therefore $E_{1/2}$ should be treated as an unknown parameter of the experiment together with k and α.

A further objective of this work was to obtain confidence intervals for the expectation values of the kinetic parameters. Typically in experiments of this type uncertainty is estimated by estimating the coefficient of variation of the current response and assigning that coefficient of variation to the derived parameters, because more realistic procedures have not been available. The procedure presented by O'Dea et al. [1] has the merit of computational simplicity and thus provides a well-defined quantity that can be used by the experimenter as a working figure of merit during the course of experiments. The procedure of Lane et al., which provides conventional confidence intervals with known confidence bound, relies on quadratic approximation of the model, which should be adequate for well-behaved response surfaces.

Recent advances in theory and in computational capabilities raise the possibility of fully quantitative theoretical descriptions of at least some classes of electrochemical reactions. Theoretical developments can be guided and tested using accurate data that have been analyzed using appropriate statistical techniques.

References

[1] O'Dea, John J.; Janet Osteryoung, and R. A. Osteryoung, J. Phys. Chem. 1983, 87, 3911–3918.