Use of higher overvoltages in coulostatic kinetic measurements

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Use of Higher Overvoltages in Coulostatic Kinetic Measurements

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FOR A FIRST ORDER electrode reaction, the rate of electron transfer is given by the following well known equation (1):

$$i_f = nFAk_sC_O^{*(1-\alpha)}C_R^{*\alpha}\{(C_O/C_O^*)\exp(-\alpha nF\eta/RT) -$$
$$(C_R/C_R^*)\exp[(1 - \alpha)nF\eta/RT]\} \quad (1)$$

where i_f is the faradaic current; α, the transfer coefficient; k_s, the standard electrochemical rate constant; η, overpotential; C_R and C_O, surface concentration of reduced and oxidized species; C_R^* and C_O^*, bulk concentrations of reduced and oxidized species; and the other terms have their usual meaning.

When diffusion also must be considered, this equation constitutes a boundary condition for solution of the Fick diffusion equations. Because the relationship between potential and concentration in Equation 1 is nonlinear, in general the Fick boundary value problem cannot be solved analytically. Thus in deriving the basic equation describing simultaneous charge transfer and diffusional relaxation in the coulostatic method, it is common practice to linearize Equation 1 by expanding the exponentials in a Taylor series and retaining only the first two terms (2, 3). For this approximation to be valid the argument of the exponentials must be much less than 1. This has limited all perturbation techniques using the linearized equation to small potential excursions of about $5/n$ mV.

By solving the boundary value problem without introducing linearization, Nicholson (4) has found that for the case of pure diffusional relaxation, the exponential terms are of minor importance in the final result so that larger overpotentials can be used without increasing the error level. The results agree with linearized theory for overpotentials as large as $25/n$ mV.

To determine if the same is true of the case for simultaneous charge transfer and diffusional relaxation, it was decided to solve the general equation for this case without introducing linearization.

The boundary value problem to be solved is the following:

$$\partial C_O/\partial t = D_O(\partial^2 C_O/\partial x^2) \quad (2)$$

$$\partial C_R/\partial t = D_R(\partial^2 C_R/\partial x^2) \quad (3)$$

$$t = 0, x > 0, C_O = C_O^*, C_R = C_R^* \quad (4)$$

$$t > 0, x \to \infty, C_O \to C_O^*, C_R \to C_R^* \quad (5)$$

$$t > 0, x = 0, D_O(\partial C_O/\partial x) + D_R(\partial C_R/\partial x) = 0 \quad (6)$$

$$C_O/C_R = \exp[(nF/RT)(E - E°)] =$$
$$(C_O^*/C_R^*)\exp[nF\eta/RT] \quad (7)$$

$$D_O(\partial C_O/\partial x) = (C_d/nFA)d\eta/dt - (C_d/nFA)\eta_{t=0}\delta(\theta, t) \quad (8)$$

The following parameters have not been defined previously: C_d is the double layer capacity, $\eta_{t=0}$ is the maximum potential developed across the double layer before relaxation occurs, D_O and D_R the diffusion coefficients for oxidized and reduced

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(2) P. Delahay, *J. Phys. Chem.*, **66**, 2204 (1962).
(3) W. H. Reinmuth, ANAL. CHEM., **34**, 1272 (1962).
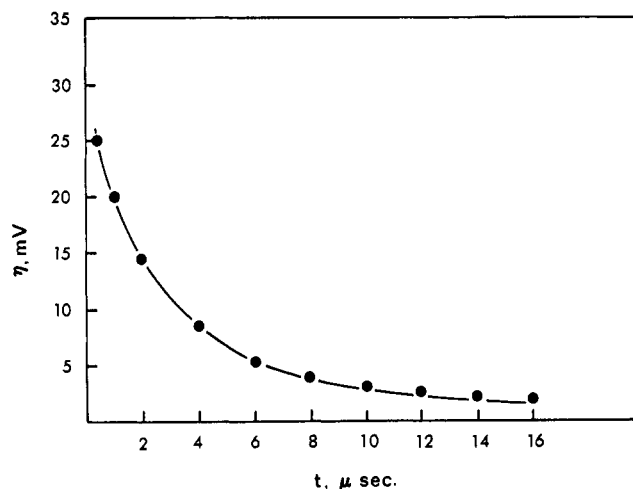(4) R. S. Nicholson, *ibid.*, **37**, 667 (1965).

Figure 1. Comparison of linear coulostatic decay curve with experimental data for the hexacyanoferrate (III/II) couple, $C_O = C_R = 1 \times 10^{-5}$ m/cm^3, $C_d = 28.6$ μF/cm^2, $I° = 0.235$ A/cm^2, experimental, – calculated from Equation 20

species, and $\delta(\theta,t)$ is the Dirac delta function. The integral equation representations of Equations 2 and 3 are (5):

$$C_{O_{x=0}} = C_O^* - \frac{1}{nFA(\pi D_O)^{1/2}} \int_0^t i(\tau)d\tau/\sqrt{t - \tau} \quad (9)$$

$$C_{R_{x=0}} = C_R^* - \frac{1}{nFA(\pi D_R)^{1/2}} \int_0^t i(\tau)d\tau/\sqrt{t - \tau} \quad (10)$$

where τ is a dummy variable of integration. The flux can also be defined as:

$$D_O(\partial C_O/\partial x) = k_f C_O(0, t) - k_b C_R(0, t) \quad (11)$$

where

$$k_f = k_s\exp[(-\alpha nF/RT)(E - E°)] \quad (12)$$

and

$$k_b = k_s\exp[(1 - \alpha)(nF/RT)(E - E°)] \quad (13)$$

By combining Equations 7, 8, 9, 10, 11, 12, and 13 and rearranging, the following equation is obtained:

$$\tau_c(d\eta/dt) - \tau_c\eta_{t=0}\delta(\theta, t) =$$

$$\exp[(-\alpha nF/RT)\eta]\left\{RT/nF - \tau_0^{1/2}/\pi^{1/2}\right.$$

$$\left[\int_0^t d\eta/dt\, d\tau/\sqrt{t - \tau} - \eta_{t=0}\int_0^t \delta(\theta, t)d\tau/\sqrt{t - \tau}\right] -$$

$$RTn/F \exp[(nF/RT)\eta] - \exp[(nF/RT)\eta]\tau_R^{1/2}/\pi^{1/2} \times$$

$$\left[\int_0^t d\eta/dt\, d\tau/\sqrt{t - \tau} - \eta_{t=0}\int_0^t \delta(\theta, t)d\tau/\sqrt{t - \tau}\right]\right\}$$

$$(14)$$

where

$$\tau_c = RTC_d/nFi_o \quad (15)$$

(5) W. H. Reinmuth, *ibid.*, **34**, 1446 (1962).

τ_c/τ_d	50		5		1		0.5		0.05	
t/τ_d	Linear Eq 20	Nonlinear Eq 19	Linear Eq 20	Nonlinear Eq 19	Linear Eq 20	Nonlinear Eq 19	Linear Eq 20	Nonlinear Eq 19	Linear Eq 20	Nonlinear Eq 19
0.01	0.999	0.999	0.998	0.998	0.991	0.991	0.982	0.982	0.927	0.929
0.04	0.999	0.999	0.992	0.992	0.966	0.967	0.941	0.942	0.838	0.840
0.16	0.997	0.997	0.970	0.970	0.886	0.888	0.825	0.827	0.692	0.695
0.36	0.993	0.993	0.936	0.939	0.786	0.787	0.705	0.707	0.583	0.586
0.64	0.987	0.987	0.892	0.894	0.686	0.689	0.599	0.601	0.499	0.502
1.00	0.980	0.980	0.841	0.842	0.593	0.595	0.513	0.514	0.435	0.437
2.25	0.957	0.958	0.698	0.699	0.417	0.420	0.365	0.369	0.326	0.328
4.00	0.925	0.926	0.555	0.557	0.309	0.313	0.279	0.283	0.256	0.258
6.25	0.887	0.889	0.430	0.432	0.242	0.247	0.225	0.227	0.205	0.207
9.00	0.842	0.845	0.332	0.335	0.198	0.202	0.188	0.190	0.168	0.169

$$i_o = nFA\ C_O^* k_s \exp[(-\alpha nF/RT)\ (E_i - E^\circ)] \qquad (16)$$

$$E_i = E - \eta$$

$$\tau_0^{1/2} = RT\ C_d/\pi^2 F^2 A(1/C_O D_O^{1/2}) \qquad (17)$$

$$\tau_R^{1/2} = RT\ C_d/n^2 F^2 A(1/C_R D_R^{1/2}) \qquad (18)$$

Now substituting $\psi(t) = (nF/RT)\eta$ and $\psi_i = (nF/RT)\eta_{t=0}$ into Equation 14, replacing t with λ, and integrating from zero to t, a nonlinear integral equation is obtained:

$$2\sqrt{t\psi_i} - \int_0^t \psi(t)d\lambda/\sqrt{t - \lambda} =$$

$$\pi^{1/2}\tau_c \int_0^t \frac{\exp[\alpha\psi(\lambda)][d\psi(\lambda)/d\lambda]d\lambda}{\tau_0^{1/2} + \tau_R^{1/2}\exp[\psi(\lambda)]} -$$

$$\pi^{1/2}\tau_c\psi_i \int_0^t \frac{\exp[\alpha\psi(\lambda)]\delta(\theta, \lambda)d\lambda}{\tau_0^{1/2} + \tau_R^{1/2}\exp[\psi(\lambda)]} +$$

$$\pi^{1/2} \int_0^t \frac{[\exp(\psi(\lambda)) - 1]d\lambda}{\tau_0^{1/2} + \tau_R^{1/2}\exp[\psi(\lambda)]} \qquad (19)$$

By reducing this to dimensionless form and using the method of numerical solution (4), curves can be obtained which follow this equation.

The linear equation derived by Delahay (2) and Reinmuth (3):

$$\eta = \eta_{t=0}(\gamma - \beta)^{-1}[\gamma \exp(\beta^2 t)\mathrm{erfc}(\beta t^{1/2}) -$$

$$\beta \exp(\gamma^2 t)\mathrm{erfc}(\gamma t^{1/2})] \qquad (20)$$

where $\beta,\gamma = \tau_d^{1/2}/2\tau_c \pm (\tau_d/4\tau_c^{-1})^{1/2}/\tau_c^{1/2}$ and $\tau_d^{1/2} = \tau_0^{1/2} + \tau_R^{1/2}$

can also be solved to give similar curves. Typical results from computer solution of the nonlinear integral Equation 19 and Equation 20 of Delahay and Reinmuth are given in

Table I for various rations of τ_c to τ_d. This ratio has been shown to be a very useful indicator of the rate controlling process and of the most efficient data analysis method (6). The examples given in Table I cover the range from almost complete charge transfer control $(\tau_c/\tau_d) = 50)$ to almost complete diffusion control $(\tau_c/\tau_d = 0.05)$. For $n = 1$ and $\eta_{t=0}\ 25.6$ mV, the linear and nonlinear relaxation curves agree within 2%; thus it appears that higher overpotentials can be used in the coulostatic method where either or both charge transfer and diffusional relaxation are occurring without introducing error.

To test the use of the linearized equation for large overpotentials, the hexacyanoferrate (III)/(II) couple on platinum was studied. Experimental conditions were as given by Daum and Enke (7). Overpotentials from 4 to 25 mV were used and the capacitance and exchange current calculated using a computer curve fitting program for Equation 20. Figure 1 indicates the kind of results which were obtained at higher overpotentials. This result is essentially the same as those obtained using low overpotentials. Thus overpotentials as high as $25/n$ mV can be used in the coulostatic method and accurate results obtained.

ACKNOWLEDGMENT

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