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Effect of ohmic losses on potentiostatic transient response of a reversible redox system*

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The ohmic potential drop between the working and reference electrodes plays an important role in the early stage of the voltage-step transient process. The non-linear effect of the ohmic drop on the transient currents is calculated for large voltage steps, assuming reversible behaviour (negligible surface overpotential) of the redox couple O + ne = R.

Nomenclature

A	area of working electrode (m^2)
a_C	Cottrell coefficient ($A\,s^{1/2}\,m^{-2}$), Equation 10a
B	parameter of Cottrell asymptote, Equation 10c
c_k	concentration field of kth component ($mol\,m^{-3}$)
D_k	diffusion coefficient of kth component ($m^2\,s^{-1}$)
$d_x^{-1/2}$	semiintegral, $d_x^{-1/2}F(x) = \pi^{-1/2}\int_0^x \times (x - s)^{-1/2}F(s)\,ds$
f	parameter of Cottrell asymptote, Equation 10b
I	current (A)
I_0	initial current ($\equiv -U/R_w$) (A)
i	current density ($\equiv I/A$) ($A\,m^{-2}$)
j_k	diffusion flux density of kth component ($mol\,m^{-2}\,s^{-1}$)
r_w	radius of a disc electrode (m)
P	normalized overpotential ($\equiv FU/RT$)
R_w	ohmic resistance adjoined to working electrode (Ω)
t	time from the start (s)
t_0	initial lag time ($\equiv (AR_w\alpha_c/U)^2$) (s)
U	constant voltage step from equilibrium (V)
η_c	concentration overpotential (V)
κ	electroconductivity of bulk solution ($\Omega^{-1}\,m^{-1}$)

Subscripts

k	kth component
O	cathodic depolarizer
R	anodic depolarizer

Superscripts

w	surface of working electrode
b	bulk of solution

1. Introduction

The transient response induced by a voltage step can yield important physicochemical data about electrolytic processes [1]. In particular, the coefficients of diffusion for a reversible redox couple can be determined using this method.

The phrase "potentiostatic transient" expresses an idealized concept rather than an experimental procedure, as the ohmic drop between the working and reference electrodes cannot be completely compensated in the early stage of a transient process, when rapid changes of relatively high currents occur. Therefore, the more correct approach to treating the transient data is based on the voltage-step transient model which includes ohmic losses [1, 2]. Due to non-linearity of the electrochemical relations, such as the Nernst equation or Volmer-Butler kinetics, the transient process model including ohmic losses is inevitably non-linear. Only the linearized approximate solution to the problem is known [1, 2] and is limited to very low overpotentials. It is the purpose of the present paper to analyse the effect of ohmic losses over the full span of overpotentials including the region of limiting diffusion currents which is of particular importance in electrodiffusion diagnostics of flow [3].

2. Theory

2.1. *Statement of the problem*

We consider here the one-dimensional unsteady simultaneous diffusion of the two components, k = O, R, of a reversible redox couple, O + ne = R, between a polarizable working electrode (located in the plane z = 0) and a semi-infinite immobile medium. Starting with the equilibrium state, $c_k = c_k^b$ and I = 0, at time t < 0, the transient process is induced by a voltage step, U, between the working electrode and a non-polarized electrode of the same type, located at a fixed point outside the diffusion layer. During the transient process, U is kept constant.

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Under these assumptions, U is the sum of the ohmic drop, $-IR_{\mathrm{w}}$, and the concentration overpotential, η_{c}, between the two electrodes of the same type,

$$U = \eta_{\mathrm{c}} - IR_{\mathrm{w}} \tag{1}$$

$$(c_{\mathrm{O}}^{\mathrm{w}}/c_{\mathrm{O}}^{\mathrm{b}})(c_{\mathrm{R}}^{\mathrm{w}}/c_{\mathrm{R}}^{\mathrm{b}})^{-1} = \exp\left(\frac{nF}{RT}\eta_{\mathrm{c}}\right) \tag{2}$$

2.2. *Mathematical model*

Transient diffusion of the kth component in a semi-infinite immobile medium is governed by the Cottrellian boundary-value problem:

$$\partial_t c_k = D_k \partial_{zz}^2 c_k \tag{3}$$

$$c_k \longrightarrow c_k^{\mathrm{b}}\ (=\mathrm{const}) \qquad \text{for } t \longrightarrow \mathrm{O}_+ \text{ or } z \longrightarrow \infty \tag{4a}$$

$$c_k = c_k^{\mathrm{w}}(t) \qquad \text{for } t > 0 \text{ and } z = 0 \tag{4b}$$

$$j_k(t) = -D_k \partial_z c_k| \qquad z = 0 \tag{5}$$

The general solution to the single-component problem provides the following integral relations between the wall concentration $c_k^{\mathrm{w}}(t)$ and the diffusion flux density $j_k(t)$:

$$(D_k)^{1/2}(c_k^{\mathrm{w}}(t) - c_k^{\mathrm{b}}) = d_t^{-1/2} j_{k'} \tag{6a}$$

$$j_k = d_t^{1/2}(D_k)^{1/2}(c_k^{\mathrm{w}}(t) - c_k^{\mathrm{b}}). \tag{6b}$$

In real multicomponent problems, these boundary-valued quantities for various components are interrelated by additional boundary conditions, specified at the surface of the working electrode.

We limit ourselves to reversible redox systems, $\mathrm{O} + ne = \mathrm{R}$, for which the surface concentrations are interrelated by stoichiometric constraints $-j_{\mathrm{O}} = j_{\mathrm{R}} = I/nFA$. That is,

$$\begin{aligned}(D_{\mathrm{O}})^{1/2}[c_{\mathrm{O}}^{\mathrm{b}} - c_{\mathrm{O}}^{\mathrm{w}}(t)] &= -(D_{\mathrm{R}})^{1/2}[c_{\mathrm{R}}^{\mathrm{b}} - c_{\mathrm{R}}^{\mathrm{w}}(t)] \\ &= d_t^{-1/2}(I/nFA)\end{aligned} \tag{7}$$

and by the local equilibrium condition (Nernst equation),

$$c_{\mathrm{O}}^{\mathrm{w}}(t)/c_{\mathrm{R}}^{\mathrm{w}}(t) = (c_{\mathrm{O}}^{\mathrm{b}}/c_{\mathrm{R}}^{\mathrm{b}}) \exp\left[\frac{nF}{RT}(U + IR_{\mathrm{w}})\right] \tag{8}$$

For the strictly potentiostatic transient process, $R_{\mathrm{w}} = 0$, the problem was solved by Cottrell [1]:

$$i = a_{\mathrm{C}}(\pi t)^{-1/2} \tag{9}$$

$$a_{\mathrm{C}} \equiv \frac{nF(\exp(P) - 1)}{\exp(P)/(c_{\mathrm{O}}^{\mathrm{b}} D_{\mathrm{O}}^{1/2}) + 1/(c_{\mathrm{R}}^{\mathrm{b}} D_{\mathrm{R}}^{1/2})} = nFc_{\mathrm{O}}^{\mathrm{b}} D_{\mathrm{O}}^{1/2} f \tag{10a}$$

$$f \equiv \frac{\exp(P) - 1}{\exp(P) + B} \tag{10b}$$

$$B \equiv c_{\mathrm{O}}^{\mathrm{b}} D_{\mathrm{O}}^{1/2}/(c_{\mathrm{R}}^{\mathrm{b}} D_{\mathrm{R}}^{1/2}) \tag{10c}$$

When the ohmic drop is taken into consideration, the problem becomes non-linear due to the exponential term in Equation 8. Introducing the normalized concentration driving force W, normalized flux N, and the appropriate time variable T,

$$W \equiv \frac{1}{f}(1 - c_{\mathrm{O}}^{\mathrm{w}}/c_{\mathrm{O}}^{\mathrm{b}}) = \frac{1}{Bf}(1 - c_{\mathrm{R}}^{\mathrm{w}}/c_{\mathrm{R}}^{\mathrm{b}}) \tag{11a}$$

$$N \equiv I/I_0 \tag{11b}$$

$$T \equiv t/t_0 \tag{11c}$$

into the Equations 7 and 8, we obtain the system of two equations

$$W(T) = d_T^{-1/2} N(T) \tag{12a}$$

$$N(T) = 1 - \frac{1}{P}\ln\left(\frac{1 + BfW(T)}{1 - fW(T)}\right) \tag{12b}$$

which should be solved simultaneously for the two adjustable parameters P, B. For P $\ll$ 1, the problem becomes asymptotically linear, $N \approx 1 - W$, with the well-known explicit solution [1, 2]:

$$N(T) \approx \exp(T)\,\mathrm{erfc}(T^{1/2}). \tag{13}$$

The asymptote for $T \ll 1$ can be found, starting with the obvious asymptotes $N \approx 1$, $W \approx 2(T/\pi)^{1/2}$, and expanding N into a power series:

$$N(T) \approx 1 - a_1 T^{1/2} - a_2 T - \dots \tag{14}$$

$$a_1 = \frac{2}{\sqrt{\pi}}(1 + B)\frac{f}{P} \tag{15a}$$

$$a_2 = -a_1^2\left[\frac{\pi}{4} - \left(\frac{1 - B}{1 + B}\right)\left(\frac{P}{2}\right)\right] \tag{15b}$$

Using the obvious zero-order asymptotic estimates of W for both $T \ll 1$ ($W \approx 2(T/\pi)^{1/2}$) and $T \gg 1$ ($W \approx 1$), the following asymptotic structure can be found for N at $T \gg 1$:

$$N(T) \approx (\pi T)^{-1/2}(1 + b_1 T^{-1} + b_2 T^{-2} + \dots). \tag{16}$$

The actual values of b_1, b_2 cannot be found through an asymptotic analysis as they depend on the entire course of $N = N(T)$.

2.3. *Numerical solution*

A standard finite-difference method was used to compute the semi-integral in Equation 12a, see the discrete scheme R2 in [4, p. 147]. The constant step $\mathrm{d}T = 0.01$ was sufficient to achieve an accuracy of five decimal digits in $N(T)$. The values of $N(T)$ for several first mesh points were estimated using Equation 14. With a guess $N^j = N^j(T)$, an improved course $N^{j+1} = N^{j+1}(T)$ was computed using the relaxation scheme

$$W = d_T^{-1/2} N^j \tag{17a}$$

$$N^{j+1/2} = 1 - \frac{1}{P}\ln\left(\frac{1 + BfW}{1 - fW}\right) \tag{17b}$$

$$N^{j+1} = (N^{j+1/2} + \mu N^j)/(1 + \mu) \tag{17c}$$

The optimum values of the relaxation coefficient, μ, were found to be close to 0.2 at low and medium P.

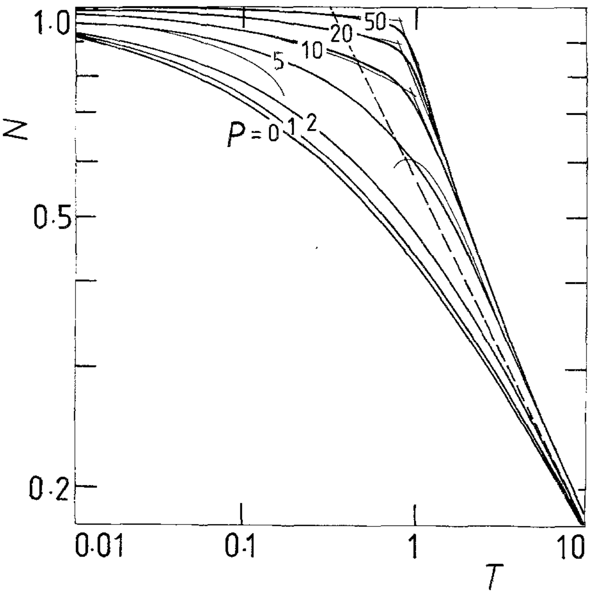

Fig. 1. Theoretical courses for N against T for the particular case $B = 1$. Thick solid lines – numerical results; thin solid lines – asymptotes according to Equations 14 and 16; dashed line – Cottrellian asymptote, $N = (\pi T)^{-1/2}$.

Five iterations were sufficient for stabilizing six decimal digits in N. For $P \gg 5$, the iteration process converged rather slowly and required higher values of the relaxation coefficient.

The detailed computations were undertaken for the most common case $B = 1$. It should be noted that the courses $N = N(T)$ for $-P$ and P are identical for this particular case. The resulting courses of $N = N(T)$ are shown in Fig. 1. The most important for applications is the asymptotic representation (Equation 16) for $T \gg 1$ which expresses slight deviations from the Cottrell asymptote, Equation 9. The values b_1, b_2 were found by fitting the asymptotic expansion (16) on the numerical data for $T \geq 1$. The resulting values for $P > 2$ were satisfactorily correlated in the following way:

$$b_1 = (f^3 - 1)/2, \qquad (18a)$$

$$b_2 = -4.3 b_1/P \qquad (18b)$$

3. Comparison with experimental results

3.1. *Experimental conditions*

The voltage-step transient experiments were carried out with the aqueous solution containing 55% of saccharose, 25 mol m^{-3} $K_3Fe(CN)_6$, 25 mol m^{-3} $K_4Fe(CN)_6 \cdot H_2O$, and 57 mol m^{-3} K_2SO_4. The standard rotating disc electrode, made from platinum wire, $r_w = 1$ mm, was used as the working electrode. The effective area of the working electrode during an early stage of the transient process was estimated to be higher by 5% than the macroscopic area, $A = 1.05\pi r_w^2$. The geometrical arrangement of electrolytic cell and other technical details are described in [5]. It should be noted that only the early stage of the transient process is considered here. Its course does not depend on the rotation speed, including the extremum case of the immobile working disc electrode. (For example, see [5]).

All the electrodiffusion experiments were conducted at constant temperature 298.4 K. The coefficient of diffusion for the cathodic depolarizer, $D_O = 52.6 \times 10^{-12}\,m^2 s^{-1}$, was determined using the rotating disc electrode under steady state limiting-current conditions [5]. The electroconductivity, $\kappa = 0.16\,\Omega^{-1} m^{-1}$, was determined using the standard conductometric technique.

3.2. *Estimate of ohmic resistance*

The simplest estimate of the ohmic resistance for a disc working electrode in the cell with a large-area counter electrode follows from the theory of primary current distribution [6, p. 344]:

$$R_w = 1/(4\kappa r_w) = 1.55\,k\Omega. \qquad (19)$$

According to this concept, the ohmic potential loss is concentrated in a small semispherical volume around the working electrode. It was checked experimentally that the transient currents were independent of the location of the reference electrode, including the two-electrode circuit as a particular case.

3.3. *Results*

Only the critical period of the transient process, with ohmic and diffusion resistances of the same order of magnitude is shown in the Fig. 2. The short-time data ($30\,\mu s < t < 1$ ms) correspond to the constant-current regime, $I = I_0$, and will be discussed later. The long-time data ($0.2\,s < t < 10\,s$) have been previously published and analysed in [5]. In particular, the period $0.3\,s < t < 1\,s$ corresponds to the

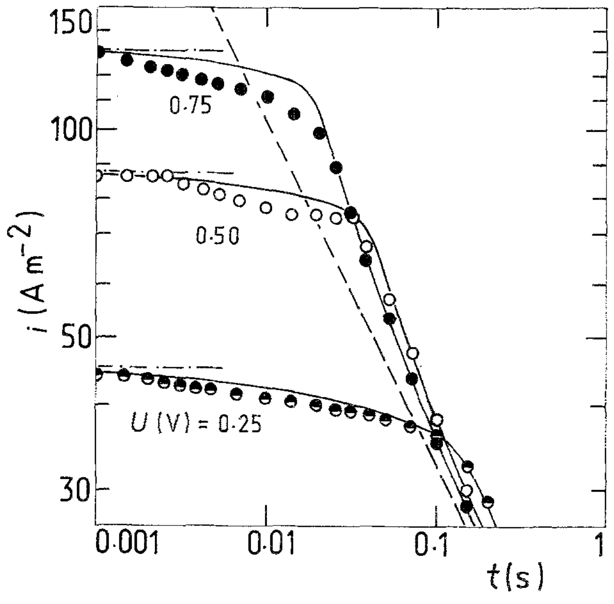

Fig. 2. Experimental transient data for 55% sucrose solution; the applied voltages (0.25, 0.50, 0.70 V) correspond to $P = 10, 20, 30$, respectively. Thick solid lines – theoretical courses ($B = 1$); dashed line – common Cottrellian asymptote for $P \gg 5$; dash-and-dotted lines – initial currents.

well-developed Cottrellian limiting-diffusion region with $a_C = nFc_O^b D_O = 18.1\,\mathrm{A\,s^{1/2}\,m}^{\ 2}$. The corresponding value of D_O is in close agreement with the aforementioned steady state result.

During a short initial period, $t \ll t_0$, the current is controlled by the ohmic losses and deviates only slightly from the initial value, I_0. The experimental evidence of the prevailing ohmic control in the initial period is the proportionality between the initial current, I_0, and the applied voltage, U. The three runs, $U = 0.75$, 0.5, and 0.25 V, with the corresponding initial currents, $I_0 = 432$, 290, and 148 μA, provide the effective resistance $R_w = 1.7\,\mathrm{k\Omega}$, which is very close to the theoretical estimate given in Equation 19.

3.4. *Discussion*

The most delicate question in comparing a theoretical prediction of current densities with experimental data is the determination of the effective area, A, of the electrode surface. As argued in [5], this parameter can be higher than the macroscopic area because of the surface roughness. This effect can be analysed quantitatively by introducing the enhancement factor $E \equiv A/\pi r_w^2$ and considering its dependence on the actual current density [5].

The data presented in Fig. 2, were obtained assuming the constant enhancement factor, $E = 1.05$, in the region $t < 0.2$ s. Within the range of the pure Cottrellian regime, $0.2 < t < 0.5$, this estimate is in fairly good agreement with the experimentally obtained roughness characteristics of the electrode used (referred to as the BLUE electrode in [5]). At shorter times, the assumption $E = 1.05$ does not agree with the roughness characteristics, given in [5], but it fits the actual data on the transient currents very well.

The theoretical courses of the transient currents for high voltages, $|P| > 2$, approach the Cottrell asymptote, $N \approx (\pi T)^{-1/2}$, from above, instead of from below. This "overshooting" effect is relatively strong – the maximum overshoot, apparent in Fig. 1, is approximately 50%. Neglecting this effect in [5] resulted in overestimating the enhancement factors in the region of pronounced overshoot, $t < 0.2$ s. For the same reason, there is a discrepancy between the data in Fig. 2 here and Fig. 2.2 of [7], which both are based on the same primary experimental material.

4. Conclusions

The comparison of the linear asymptote (Equation 13) with the numerically determined courses of $N = N(T)$ indicates that the linear asymptote is valid, with the deviations in N less than 1%, up to the values $|P| < 0.5$, i.e. $|U| < 12$ mV. This limit is slightly higher than the value $2 \div 5$ mV suggested in [2]. For $|P| = 1$, the deviations in N are roughly 3% (see Fig. 1).

The essential purpose of the presented theory was to map the effect of the ohmic drop under conditions close enough to the limiting diffusion current regime. With the requirement $f > 0.999$, this region is limited by the condition $|P| > 8$. In this region, the transient currents approach the Cottrellian asymptote (Equation 9) from above. This surprising phenomenon throws some doubts on the oversimplified approach [5, 7] of estimating the overall transport resistance by summing the Cottrellian and ohmic resistances.

References

[1] D. D. McDonald, 'Transient Techniques in Electrochemistry', Plenum Press, New York (1981).

[2] W. Vielstich and P. Delahay, *J. Am. Chem. Soc.* **79** (1957) 1874.

[3] O. Wein, P. Mitschka and V. V. Tovchigrechko, *Chem. Eng. Commun.* **32** (1985) 153.

[4] K. B. Oldham and J. Spannier, 'The Fractional Calculus', Academic Press, New York (1974).

[5] O. Wein and F. H. Assaf, *Collect. Czech. Chem. Commun.* **52** (1986) 848.

[6] J. S. Newman, 'Electrochemical Systems', Prentice Hall, Englewood Cliffs, NJ (1973).

[7] N. A. Pokryvaylo, O. Wein and N. D. Kovalevskaya, 'Electrodiffusion Diagnostics of Flow' (in Russian), Nauka i Tekhnika, Minsk (1988).