Short Communication

Surface concentration nonuniformities resulting from chronoamperometry of a reversible reaction at an ultramicrodisk electrode

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ABSTRACT

The chronoamperometric experiment at a disk electrode was simulated, assuming a reversible reaction. When the diffusion coefficients of the two substances involved are different, there appears a surface concentration non-uniformity in the radial direction, exhibiting a maximum effect in time. At long times, the nonuniformity disappears.

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1. Introduction

We report here results of simulations of chronoamperometry at an ultramicrodisk electrode, the reaction being the reversible reduction of substance A to B:

$$A + e^- \rightleftharpoons B. \qquad (1)$$

Note that this is not a study under limiting current conditions, where concentrations are forced to zero at the electrode, although at the very negative applied potentials (see later) that of species A is close to zero. The focus is on whether and how concentrations of both A and B on the disk surface vary with the radius r, for equal and unequal diffusion coefficients D_A and D_B of substances A and B, respectively. In a paper by Bond et al. [1], it is mentioned that the surface concentrations are uniform at steady state for a reversible system, irrespective of the relative diffusion coefficients. Streeter and Compton [2] studied this system but for equal diffusion coefficients, where (as will also be seen below) concentrations over the disk are uniform at all times; that is, on the disk surface and at any radius r between the disk centre and edge.

The surface concentrations for this geometry - and presumably for all electrodes with an edge, such as bands etc. - vary with position on the surface, and in this Nernstian reaction system, they also vary with time. The latter is also true for uniformly accessible electrodes such as (hemi)spherical or long (hemi)cylinders, but these do not show surface nonuniformities.

The experiment to be simulated is a jump, at time zero, to potential E. The dimensionless transport equations are, for cylindrical coordinates,

$$\begin{aligned}
\frac{\partial A}{\partial T} &= \frac{\partial^2 A}{\partial R^2} + \frac{1}{R}\frac{\partial A}{\partial R} + \frac{\partial A}{\partial Z}, \\
\frac{\partial B}{\partial T} &= d_B \left(\frac{\partial^2 B}{\partial R^2} + \frac{1}{R}\frac{\partial B}{\partial R} + \frac{\partial B}{\partial Z} \right),
\end{aligned} \qquad (2)$$

where A and B are the normalised concentrations of, respectively, A and B, relative to the bulk concentration of A, T is the time t normalised as $T = D_A t/a^2$; a is the disk radius, $R = r/a$ is the dimensionless radius and $Z = z/a$ the dimensionless vertical distance above the disk. The symbol $d_B = D_B/D_A$ represents the dimensionless diffusion coefficient for B, and this is a critical parameter. This geometry will now be called RZ. Boundary conditions are

$$\begin{array}{ll}
T = 0, \text{all } R, Z: & A = 1, B = 0 \\
T > 0, 0 \le R \le 1, Z = 0: & A/B = \exp(p) \\
Z = 0, 0 \le R \le 1: & \frac{\partial A}{\partial Z} + d_B \frac{\partial B}{\partial Z} = 0 \text{ (flux equality)} \\
R = 0, Z > 0: & \frac{\partial A}{\partial R} = \frac{\partial B}{\partial R} = 0 \\
R > 1, Z = 0: & \frac{\partial A}{\partial Z} = \frac{\partial B}{\partial Z} = 0 \\
R \to \infty, Z \to \infty: & A = 1, B = 0
\end{array} \qquad (3)$$

having defined the dimensionless potential $p = \frac{n\mathcal{F}}{\mathcal{R}\mathcal{T}}(E - E^0)$, E^0 being the standard potential for the reaction and n, $\mathcal{F}$, $\mathcal{R}$ and $\mathcal{T}$ having their usual meanings.

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Table 1
Surface concentrations of A at the disk centre ($R=0$) by which the curves in Fig. 1 were normalised, for the same set of parameters.

d_B	$p=0$	$p=-1$	$p=-3$	$p=-10$
0.1	0.833	0.642	0.183	1.94×10^{-4}
0.3	0.712	0.474	0.107	1.09×10^{-4}
1	0.500	0.269	4.74×10^{-2}	4.53×10^{-5}
3	0.280	0.125	1.89×10^{-2}	1.75×10^{-5}
10	0.112	0.0443	6.22×10^{-3}	5.71×10^{-6}

We express the nonuniformity as the ratio $q(R)$ of the surface concentration of A at some radial distance R from the centre of the disk to that at the disk centre, that is

$$q(R) = A(R)/A(R = 0); \tag{4}$$

and thus, $q(1)$ expresses that ratio at the disk edge. The actual surface concentrations might have been of interest instead of this ratio, but it turned out that the curves then are visually less informative, and Table 1 shows the surface concentrations at the axial point.

Eq. (2) can be transformed into elliptic coordinates (Γ,θ) for efficiency, and we choose the transformation of Verbrugge and Baker [3],

$$\begin{aligned} R &= \cos\theta + \cosh\left(\frac{\Gamma}{1-\Gamma}\right) \\ Z &= \sin\theta + \sinh\left(\frac{\Gamma}{1-\Gamma}\right), \end{aligned} \tag{5}$$

which changes the equations to

$$\frac{\partial A}{\partial T} = \frac{1}{\sin^2\theta + \sinh^2\left(\frac{\Gamma}{1-\Gamma}\right)}\left(\frac{\partial^2 A}{\partial\theta^2} - \tan\theta\frac{\partial A}{\partial\theta} + \frac{\partial^2 A}{\partial\Gamma^2} + (1-\Gamma)^2\tanh\left(\frac{\Gamma}{1-\Gamma}\right) - 2(1-\Gamma)^3\frac{\partial A}{\partial\Gamma}\right),$$

$$\frac{\partial B}{\partial T} = \frac{d_B}{\sin^2\theta + \sinh^2\left(\frac{\Gamma}{1-\Gamma}\right)}\left(\frac{\partial^2 B}{\partial\theta^2} - \tan\theta\frac{\partial B}{\partial\theta} + \frac{\partial^2 B}{\partial\Gamma^2} + (1-\Gamma)^2\tanh\left(\frac{\Gamma}{1-\Gamma}\right) - 2(1-\Gamma)^3\frac{\partial B}{\partial\Gamma}\right).$$

$$\tag{6}$$

For details of this transformation, see [4,5]. This geometry will now be called VB.

Boundary conditions are, for VB coordinates

$$\begin{array}{ll} T=0,\,\text{all }\theta\text{ and }\Gamma: & A=1, B=0 \\ T>0,\,\theta=0,\pi/2: & \partial A/\partial\theta=0, \partial B/\partial\theta=0 \\ T>0,\,\Gamma=0: & A/B=\exp(p), \dfrac{\partial A}{\partial\Gamma} + d_B\dfrac{\partial B}{\partial\Gamma}=0 \\ \Gamma=\Gamma_{max}: & A=1, B=0. \end{array} \tag{7}$$

2. Computational

The VB grid was divided into unequal intervals, which is unusual for the transformed grid. The reason is that with equal intervals and at very short times T, results are inaccurate because concentration contours are rather parallel with the electrode and poorly resolved in VB coordinates. First we determine the maximum values of the two coordinates: for θ it is always $\pi/2$, and for Γ it is Γ_{max}, to be determined according to the
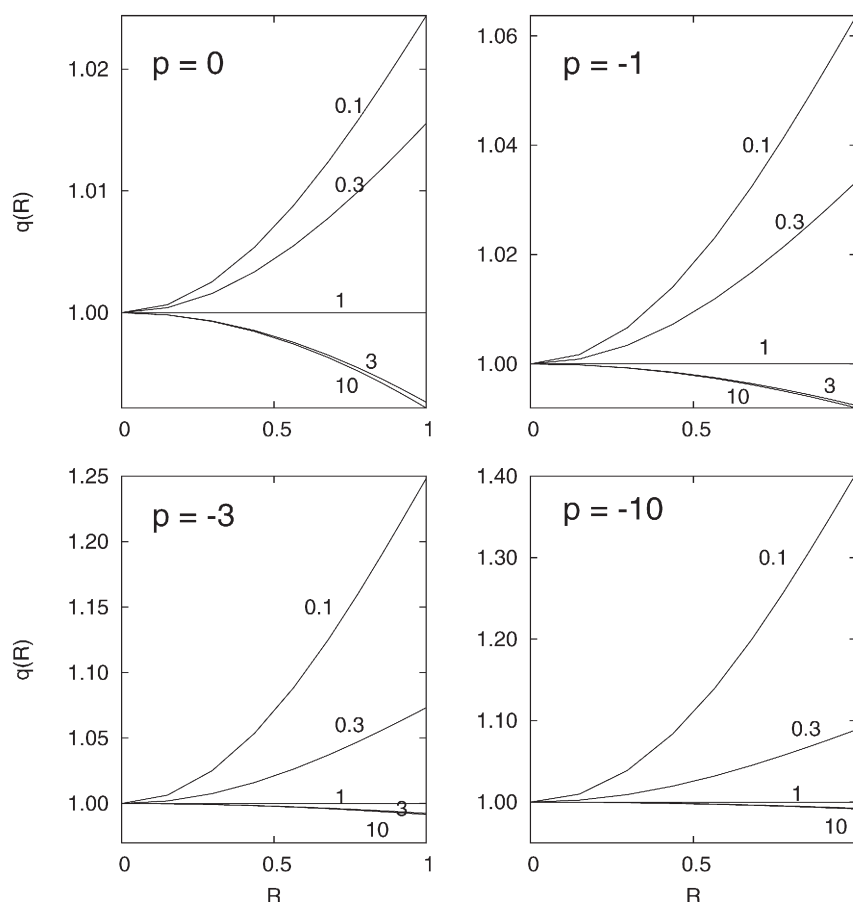

Fig. 1. Ratio $q(R)$ for a number of potentials p jumped to and diffusion coefficient ratio d_B as marked.