Cyclic Voltammetry at Micropipet Electrodes for the Study of Ion-Transfer Kinetics at Liquid/Liquid Interfaces

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Model. The geometry of a micropipet electrode is defined in cylindrical coordinates, where *r* and *z* are the coordinates in directions parallel and normal to the interface, respectively (Figure 1). The inner and outer solutions (phases 1 and 2, respectively) are denoted as phase 1 and 2. The pipet size is defined by the inner and outer tip radii, a and r_g. The inner and outer tip angles are given by θ_1 and θ_2. The pipet shaft is long enough for semi-infinite diffusion in the inner solution on a simulation time scale. The space behind the tip in the outer solution is large enough to accurately simulate back diffusion from behind the tip.

An ion with the charge z_i, i^{z_i}, is initially present only in the outer solution so that simple transfer of the ion is defined by

$$i^{z_i}\ \text{(outer solution)} \rightleftharpoons i^{z_i}\ \text{(inner solution)} \qquad (1)$$

When an ionophore with the charge z_L, L^{z_L}, forms complexes with the ion in the inner solution, the facilitated transfer is defined by

$$i^{z_i}\ \text{(outer solution)} + sL^{z_L}\ \text{(inner solution)} \rightleftharpoons iL_s^{z_i+sz_L}\ \text{(inner solution)} \qquad (2)$$

Since the ionophore is assumed to be in large excess, the facilitated transfer may be written simply as a first-order process by

$$i^{z_i}\ \text{(outer solution)} \rightleftharpoons i^{z_i}\ \text{(inner solution as ionophore complexes)} \qquad (3)$$

The transfer of an ion that is initially present only in the inner solution is not simulated in this work. Theory is available for a steady-state voltammogram as obtained for facilitated transfer of an ion in large excess in the inner solution (Figure 1a).[1, 2] When an ionophore is in large excess or absent, i.e., simple transfer, in the outer solution, the following model is applicable simply by changing the initial conditions (see eqs 10 and 11).

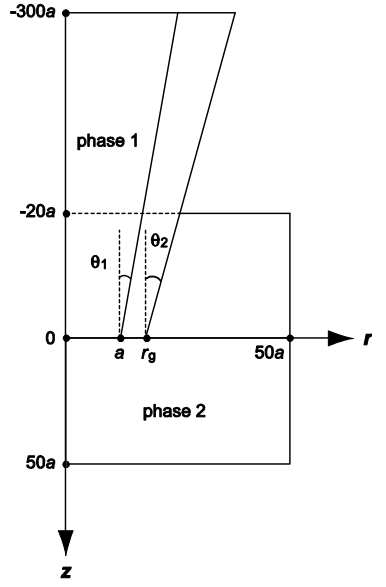

Figure 1. Defined space domain for ion transfer at a tapered micropipet electrode.

Diffusion Problem. Diffusion in the inner solution is expressed as

$$\frac{\partial c_1(r,z,t)}{\partial t} = D_1\left[\frac{\partial^2 c_1(r,z,t)}{\partial r^2} + \frac{1}{r}\frac{\partial c_1(r,z,t)}{\partial r} + \frac{\partial^2 c_1(r,z,t)}{\partial z^2}\right] \tag{4}$$

where $c_1(r,z,t)$ and D_1 are the local concentration and diffusion coefficient of the ion in the inner solution, respectively. Diffusion in the outer solution is expressed as

$$\frac{\partial c_2(r,z,t)}{\partial t} = D_2\left[\frac{\partial^2 c_2(r,z,t)}{\partial r^2} + \frac{1}{r}\frac{\partial c_2(r,z,t)}{\partial r} + \frac{\partial^2 c_2(r,z,t)}{\partial z^2}\right] \tag{5}$$

where $c_2(r,z,t)$ and D_2 are the local concentration and diffusion coefficient of the transferring ion or its complex in the outer solution, respectively.

The boundary condition at the liquid/liquid interface is given by

$$D_1\left[\frac{\partial c_1(r,z,t)}{\partial z}\right]_{z=0} = D_2\left[\frac{\partial c_2(r,z,t)}{\partial z}\right]_{z=0} = k_f c_2(r,0,t) - k_b c_1(r,0,t) \tag{6}$$

where k_f and k_b are the first-order heterogeneous rate constants for forward and reverse transfer, respectively (see eqs 1 and 3). The rate constants are given by the Butler-Volmer-type relation as[3, 4]

$$k_f = k^0 \exp[-\alpha z_i F(\Delta_2^1\phi - \Delta_2^1\phi_i^{0'})/RT] \tag{7}$$

$$k_b = k^0 \exp[(1-\alpha) z_i F(\Delta_2^1\phi - \Delta_2^1\phi_i^{0'})/RT] \tag{8}$$

where k^0 is the standard rate constant, α is the transfer coefficient, $\Delta_2^1\phi$ is the Galvani potential difference between the inner and outer solutions, and $\Delta_2^1\phi_i^{0'}$ is the formal ion-transfer potential. In cyclic voltammetry, the potential is swept linearly at the rate of v from the initial potential, $\Delta_2^1\phi_i$, and the sweep direction is reversed at the switching potential, $\Delta_2^1\phi_\lambda$, maintaining the sweep rate. The triangle potential wave is expressed as

$$\Delta_2^1\phi = \Delta_2^1\phi_i + \frac{2(\Delta_2^1\phi_\lambda - \Delta_2^1\phi_i)}{\pi}\sin^{-1}\left\{\sin\left[\frac{\pi v t}{2(\Delta_2^1\phi_\lambda - \Delta_2^1\phi_i)}\right]\right\} \tag{9}$$

The other boundary conditions are defined in Supporting Information. The initial conditions are given by

$$c_1(r,z,0) = 0 \tag{10}$$

$$c_2(r,z,0) = c_0 \tag{11}$$

where c_0 is the bulk ion concentration. A current, i, is obtained by integrating flux of the transferring ion over the liquid/liquid interface, yielding

$$i = 2\pi z_i F D_2 \int_0^a r\left[\frac{\partial c_2(r,0,t)}{\partial z}\right] dr \tag{12}$$

Simulation in the Dimensionless Form. The time-dependent diffusion problem was solved by COMSOL Multiphysics® version 3.2 (COMSOL, Inc., Burlington, MA), which applies the finite element method. Simulation accuracy of this software package for two-phase diffusion processes was demonstrated previously.[5] The diffusion problem defined above was solved in a dimensionless form (Supporting Information) such that a current response is normalized with respect to a limiting current at an inlaid disk-shaped interface, yielding i/i_{ss}, where $i_{ss} = 4z_i F D_2 c_0 a$. The normalized current is plotted with respect to $z_i\Delta\phi$ in cyclic voltammetry, where $\Delta\phi = \Delta_2^1\phi - \Delta_2^1\phi_i^{0'}$, or dimensionless time, τ, in chronoamperometry, where

$$\tau = \frac{4D_2 t}{a^2} \tag{13}$$

Features of the current response depend on the tip geometry and following dimensionless parameters

$$K = \frac{k^0 a}{D_2} \qquad \text{(dimensionless rate constant)} \tag{14}$$

$$\gamma = D_1/D_2 \qquad \text{(diffusion coefficient ratio)} \tag{15}$$

$$\sigma = \frac{a^2}{4D_2}\frac{F\nu}{RT} \qquad \text{(dimensionless scan rate)} \tag{16}$$

The diffusion problem defined above was solved using dimensionless parameters defined by

$$R = r/a \tag{17}$$

$$Z = z/a \tag{18}$$

$$C_1(R,Z,\tau) = c_1(r,z,t)/c_0 \tag{19}$$

$$C_2(R,Z,\tau) = c_2(r,z,t)/c_0 \tag{20}$$

$$\theta = \exp\left[\frac{F(\Delta_2^1\phi - \Delta_2^1\phi_i^{0'})}{RT}\right] \tag{21}$$

The other dimensionless parameters are given by eqs 13–16. Diffusion processes (eqs 4 and 5) are expressed in the respective dimensionless forms as

$$\frac{\partial C_1(R,Z,\tau)}{\partial\tau} = 0.25\gamma\left[\frac{\partial^2 C_1(R,Z,\tau)}{\partial R^2} + \frac{1}{R}\frac{\partial C_1(R,Z,\tau)}{\partial R} + \frac{\partial^2 C_1(R,Z,\tau)}{\partial Z^2}\right] \tag{22}$$

$$\frac{\partial C_2(R,Z,\tau)}{\partial\tau} = 0.25\left[\frac{\partial^2 C_2(R,Z,\tau)}{\partial R^2} + \frac{1}{R}\frac{\partial C_2(R,Z,\tau)}{\partial R} + \frac{\partial^2 C_2(R,Z,\tau)}{\partial Z^2}\right] \tag{23}$$

The values of 0.25γ and 0.25 in eqs 22 and 23 were used as dimensionless diffusion coefficients in the corresponding phases. The boundary condition at the liquid/liquid interface (eq 6) is expressed using dimensionless parameters as

$$0.25\gamma\left[\frac{\partial C_1(R,Z,\tau)}{\partial Z}\right]_{z=0} = -\frac{0.25K}{\theta^{\alpha z_i}}[\theta^{z_i}C_2(R,0,\tau) - C_1(R,0,\tau)] \quad (24)$$

$$0.25\left[\frac{\partial C_2(R,Z,\tau)}{\partial Z}\right]_{z=0} = 0.25K\theta^{(1-\alpha)z_i}[\frac{C_1(R,0,\tau)}{\theta^{z_i}} - C_2(R,0,\tau)] \quad (25)$$

Eqs 24 and 25 are equivalent to the expression of a flux boundary condition in COMSOL Multiphysics. The triangle potential wave (eq 9) is given by

$$\theta = \theta_i^{1-(2/\pi)\sin^{-1}\{\sin[\pi\sigma\tau/2\ln(\theta_\lambda/\theta_i)]\}}\theta_\lambda^{(2/\pi)\sin^{-1}\{\sin[\pi\sigma\tau/2\ln(\theta_\lambda/\theta_i)]\}} \quad (26)$$

with

$$\theta_i = \exp\left[\frac{F(\Delta_2^1\phi_i - \Delta_2^1\phi_i^{0'})}{RT}\right] \quad (27)$$

$$\theta_\lambda = \exp\left[\frac{F(\Delta_2^1\phi_\lambda - \Delta_2^1\phi_i^{0'})}{RT}\right] \quad (28)$$

The other boundary conditions and initial condition are also given using dimensionless parameters (see the attached example). The simulation gives a dimensionless current normalized with respect to a limiting current at an inlaid disk-shaped interface.

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