Electrochemical Mechanism of Ion–Ionophore Recognition at Plasticized Polymer Membrane/Water Interfaces

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Model for the EC Mechanism. The EC mechanism for facilitated IT is based on the combination of simple IT at the interface and homogeneous ion–ionophore complexation in the organic phase filled in a pipet (phase 1 in Figure 1). Specifically, simple IT is defined as

$$i^z\,(\mathrm{w}) \underset{k_{\mathrm{i,b}}}{\overset{k_{\mathrm{i,f}}}{\rightleftharpoons}} i^z\,(\mathrm{org}) \qquad (1)$$

where $k_{\mathrm{i,f}}$ and $k_{\mathrm{i,b}}$ are first-order heterogeneous rate constants. These rate constants are given by Butler-Volmer-type relations as[1, 2]

$$k_{\mathrm{i,f}} = k_\mathrm{i}^0 \exp[-\alpha_\mathrm{i} zF(E - E_\mathrm{i}^{0'})/RT] \qquad (2)$$

$$k_{\mathrm{i,b}} = k_\mathrm{i}^0 \exp[(1-\alpha_\mathrm{i}) zF(E - E_\mathrm{i}^{0'})/RT] \qquad (3)$$

The rate constants are modulated by applying to the interface a triangle potential wave between the initial potential, E_i, and the switching potential, E_λ, at a constant rate, *v*, as given by

$$E = E_\mathrm{i} + \frac{2(E_\lambda - E_\mathrm{i})}{\pi}\sin^{-1}\left\{\sin\left[\frac{\pi v t}{2(E_\lambda - E_\mathrm{i})}\right]\right\} \qquad (4)$$

Ion–ionophore complexation in the organic phase is expressed as

$$i^z\,(\mathrm{org}) + nL\,(\mathrm{org}) \underset{k_\mathrm{d}}{\overset{k_\mathrm{a}}{\rightleftharpoons}} iL_\mathrm{n}{}^z\,(\mathrm{org}) \qquad (5)$$

where k_a and k_d are association and dissociation rate constants, respectively. In the presence of the excess amount of ionophore, the homogeneous rate constants are related to each other by

$$\beta_\mathrm{n} = \frac{L_\mathrm{T}^n k_\mathrm{a}}{k_\mathrm{d}} = \frac{k_\mathrm{a}'}{k_\mathrm{d}} \qquad (6)$$

where k_a' is defined as an apparent first-order rate constant.

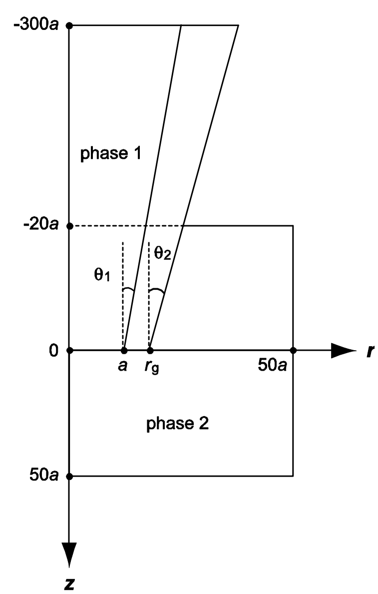

Figure 1. Defined space domain for ion transfer at a tapered micropipet electrode.

Diffusion Problem. A two-dimensional diffusion problem with the EC mechanism at a micropipet-supported organic/water interface is defined using cylindrical coordinates, where *r* and *z* are the coordinates in directions parallel and normal to the disk-shaped interface with the radius, *a*, respectively (Figure 1).[3] In the presence of the excess amount of ionophore, the diffusion of ions in free and complex forms in the inner organic solution is expressed as

$$\frac{\partial c_\mathrm{i}(r,z,t)}{\partial t} = D_\mathrm{i}\left[\frac{\partial^2 c_\mathrm{i}(r,z,t)}{\partial r^2} + \frac{1}{r}\frac{\partial c_\mathrm{i}(r,z,t)}{\partial r} + \frac{\partial^2 c_\mathrm{i}(r,z,t)}{\partial z^2}\right] - k'_\mathrm{a} c_\mathrm{i}(r,z,t) + k_\mathrm{d} c_\mathrm{c}(r,z,t) \qquad (7)$$

$$\frac{\partial c_\mathrm{c}(r,z,t)}{\partial t} = D_\mathrm{c}\left[\frac{\partial^2 c_\mathrm{c}(r,z,t)}{\partial r^2} + \frac{1}{r}\frac{\partial c_\mathrm{c}(r,z,t)}{\partial r} + \frac{\partial^2 c_\mathrm{c}(r,z,t)}{\partial z^2}\right] + k'_\mathrm{a} c_\mathrm{i}(r,z,t) - k_\mathrm{d} c_\mathrm{c}(r,z,t) \qquad (8)$$

where $c_\mathrm{i}(r,z,t)$ and $c_\mathrm{c}(r,z,t)$ are local concentrations of the free ion and its ionophore complex, respectively. The diffusion of the ion in the outer aqueous phase is described as

$$\frac{\partial c_\mathrm{w}(r,z,t)}{\partial t} = D_\mathrm{w}\left[\frac{\partial^2 c_\mathrm{w}(r,z,t)}{\partial r^2} + \frac{1}{r}\frac{\partial c_\mathrm{w}(r,z,t)}{\partial r} + \frac{\partial^2 c_\mathrm{w}(r,z,t)}{\partial z^2}\right] \qquad (9)$$

where $c_\mathrm{w}(r,z,t)$ is the local concentration of the transferring ion. The boundary condition at the DCE/water interface is given by

$$D_\mathrm{i}\left[\frac{\partial c_\mathrm{i}(r,z,t)}{\partial z}\right]_{z=0} = D_\mathrm{w}\left[\frac{\partial c_\mathrm{w}(r,z,t)}{\partial z}\right]_{z=0} = k_\mathrm{i,f} c_\mathrm{w}(r,0,t) - k_\mathrm{i,b} c_\mathrm{i}(r,0,t) \qquad (10)$$

A current response, *i*, is obtained from the flux of the transferring ion at the DCE/water solution interface as

$$i = 2\pi z_\mathrm{i} F D_\mathrm{w} \int_0^a r\left[\frac{\partial c_\mathrm{w}(r,0,t)}{\partial z}\right] dr \qquad (11)$$

where z_i is used as the ionic charge to avoid conflict with the variable for the *z* coordinate.

Simulation in the Dimensionless Form. The diffusion problem was solved in a dimensionless form using COMSOL Multiphysics version 3.5a®. Dimensionless parameters are given by

$$R = r/a \qquad (12)$$

$$Z = z/a \qquad (13)$$

$$C_\mathrm{i}(R,Z,\tau) = c_\mathrm{i}(r,z,t)/c_0 \qquad (14)$$

$$C_\mathrm{c}(R,Z,\tau) = c_\mathrm{c}(r,z,t)/c_0 \qquad (15)$$

$$C_\mathrm{w}(R,Z,\tau) = c_\mathrm{w}(r,z,t)/c_0 \qquad (16)$$

$$\tau = \frac{4 D_\mathrm{w} t}{a^2} \qquad (17)$$

$$\sigma = \frac{a^2}{4D_\mathrm{w}}\frac{Fv}{RT} \tag{18}$$

Diffusion processes coupled with ion–ionophore complexation (eqs 7 and 8) are expressed in the respective dimensionless forms as

$$\frac{\partial C_\mathrm{i}(R,Z,t)}{\partial t} = 0.25\gamma_\mathrm{i}^2\left[\frac{\partial^2 C_\mathrm{i}(R,Z,t)}{\partial R^2} + \frac{1}{R}\frac{\partial C_\mathrm{i}(R,Z,t)}{\partial R} + \frac{\partial^2 C_\mathrm{i}(R,Z,t)}{\partial Z^2}\right] - K_\mathrm{a}' C_\mathrm{i}(R,Z,t) + K_\mathrm{d} C_\mathrm{c}(R,Z,t) \tag{19}$$

$$\frac{\partial C_\mathrm{c}(R,Z,t)}{\partial t} = 0.25\gamma_\mathrm{c}^2\left[\frac{\partial^2 C_\mathrm{c}(R,Z,t)}{\partial R^2} + \frac{1}{R}\frac{\partial C_\mathrm{c}(R,Z,t)}{\partial R} + \frac{\partial^2 C_\mathrm{c}(R,Z,t)}{\partial Z^2}\right] + K_\mathrm{a}' C_\mathrm{i}(R,Z,t) - K_\mathrm{d} C_\mathrm{c}(R,Z,t) \tag{20}$$

with

$$K_\mathrm{a}' = \frac{k_\mathrm{a}' a^2}{4D_\mathrm{w}} \tag{21}$$

$$K_\mathrm{d} = \frac{k_\mathrm{d} a^2}{4D_\mathrm{w}} \tag{22}$$

Ion diffusion in the aqueous phase (eq 9) corresponds to

$$\frac{\partial C_\mathrm{w}(R,Z,t)}{\partial t} = 0.25\left[\frac{\partial^2 C_\mathrm{w}(R,Z,t)}{\partial R^2} + \frac{1}{R}\frac{\partial C_\mathrm{w}(R,Z,t)}{\partial R} + \frac{\partial^2 C_\mathrm{w}(R,Z,t)}{\partial Z^2}\right] \tag{23}$$

The boundary condition at the DCE/water interface (eq 10) is expressed using dimensionless parameters as

$$0.25\left[\frac{\partial C_\mathrm{i}(R,Z,t)}{\partial Z}\right]_{z=0} = 0.25\lambda_\mathrm{i}\theta^{(1-\alpha_\mathrm{i})}\left[\frac{C_\mathrm{w}(R,0,t)}{\theta\gamma_\mathrm{i}^2} - C_\mathrm{i}(R,0,t)\right] \tag{24}$$

$$0.25\left[\frac{\partial C_\mathrm{w}(R,Z,t)}{\partial Z}\right]_{z=0} = -\frac{0.25\lambda_\mathrm{i}}{\theta^{\alpha_\mathrm{i}}}[\theta\gamma_\mathrm{i}^2 C_\mathrm{i}(R,0,t) - C_\mathrm{w}(R,0,t)] \tag{25}$$

with

$$\lambda_\mathrm{i} = \frac{k_\mathrm{i}^0 a}{D_\mathrm{w}^{1-\alpha_\mathrm{i}} D_\mathrm{i}^{\alpha_\mathrm{i}}} \tag{26}$$

$$E_{1/2} = E_\mathrm{i}^{0\prime} + \frac{RT}{z_\mathrm{i}F}\ln\frac{D_\mathrm{i}}{D_\mathrm{w}} \tag{27}$$

The triangle potential wave (eq 5) is given by

$$\theta = \theta_\mathrm{i}^{1-(2/\pi)\sin^{-1}\{\sin[\pi z_\mathrm{i}\sigma t/2\ln(\theta_\mathrm{l}/\theta_\mathrm{i})]\}}\theta_\mathrm{l}^{(2/\pi)\sin^{-1}\{\sin[\pi z_\mathrm{i}\sigma t/2\ln(\theta_\mathrm{l}/\theta_\mathrm{i})]\}} \tag{28}$$

Eqs 24 and 25 are equivalent to the expression of a flux boundary condition in COMSOL Multiphysics. 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 as

$$I = \frac{i}{i_{\mathrm{lim}}} = \frac{p}{2}\int_0^1 R\left[\frac{\partial C_{\mathrm{w}}\left(R,0,t\right)}{\partial Z}\right]dR \qquad (29)$$

with

$$i_{\mathrm{lim}} = 4z_{\mathrm{i}}FD_{\mathrm{w}}c_0a \qquad (30)$$

REFERENCES

(1) Samec, Z.; Homolka, D.; Marecek, V. *J. Electroanal. Chem.* **1982**, *135*, 265–283.
(2) Samec, Z. *Pure Appl. Chem.* **2004**, *76*, 2147–2180.
(3) Rodgers, P. J.; Amemiya, S. *Anal. Chem.* **2007**, *79*, 9276–9285