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. Specifically, simple IT is defined as

\[ i^\text{f} (w) \sim \frac{k_{i,f}}{k_{i,b}} i^\text{f} (\text{org}) \]  

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

\[ k_{i,f} = k_i^0 \exp \left( -a_i z \frac{F(E - E_{i}^0)}{RT} \right) \]  

\[ k_{i,b} = k_i^0 \exp \left( (1 - a_i) z \frac{F(E - E_{i}^0)}{RT} \right) \]

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

\[ E = E_i + \frac{2(E_s - E_i)}{\pi} \sin^{-1} \left( \sin \left( \frac{vt}{2(E_s - E_i)} \right) \right) \]  

Ion–ionophore complexation in the organic phase is expressed as

\[ i^\text{f} (\text{org}) + nL (\text{org}) \sim \frac{k_a}{k_d} iL_n^\text{f} (\text{org}) \]  

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

\[ n = \frac{n^a k_a}{k_d} = \frac{k_a}{k_d} \]

where \( k_a \) is defined as an apparent first-order rate constant.

Diffusion Problem. A one-dimensional diffusion problem with the EC mechanism at a solid-supported membrane is defined in a linear coordinate, \( x \), vertical to the interfaces at \( x = 0 \) and also to the solid support at \( x = -l_m \), where the membrane thickness, \( l_m \), is large enough to achieve the semi-infinite diffusion of species in the membrane phase \((-l_m < x < 0)\). In the presence of the excess amount of ionophore, the diffusion of the free ion in the membrane phase is given by
\[
\frac{\partial c_i(x,t)}{\partial t} = D_i \left[ \frac{\partial^2 c_i(x,t)}{\partial x^2} \right] + k'_i c_i(x,t) + k_d c_c(x,t) \quad (-l_m < x < 0) \quad (7)
\]

where \( c_i(x,t) \) and \( c_c(x,t) \) are local concentrations of free ion and its ionophore complex, respectively. The diffusion of the complex in the membrane phase is described as

\[
\frac{\partial c_c(x,t)}{\partial t} = D_c \left[ \frac{\partial^2 c_c(x,t)}{\partial x^2} \right] + k'_c c_i(x,t) + k_d c_c(x,t) \quad (-l_m < x < 0) \quad (8)
\]

The diffusion of the target ion in the aqueous phase is expressed as

\[
\frac{\partial c_w(x,t)}{\partial t} = D_w \left[ \frac{\partial^2 c_w(x,t)}{\partial x^2} \right] \quad (0 < x) \quad (9)
\]

where \( c_w(x,t) \) is the local concentration of the transferring ion. The boundary condition at the interface is given by

\[
D_i \left[ \frac{\partial c_i(x,t)}{\partial x} \right]_{x=0} = D_w \left[ \frac{\partial c_w(x,t)}{\partial x} \right]_{x=0} = k_{i,f} c_w(0,t) - k_{i,b} c_i(0,t) \quad (10)
\]

Other boundary conditions are

\[
D_i \left[ \frac{\partial c_i(x,t)}{\partial x} \right]_{x=-l_m} = 0 \quad \text{(membrane/solid support interface)} \quad (11)
\]

\[
D_c \left[ \frac{\partial c_c(x,t)}{\partial x} \right]_{x=-l_m} = 0 \quad \text{(membrane/solid support interface)} \quad (12)
\]

\[
\lim_{x \to +\infty} c_w(x,0) = c_0 \quad \text{(simulation limit in the aqueous phase)} \quad (13)
\]

Initial conditions are

\[
c_w(x,0) = c_0 \quad (14)
\]

\[
c_i(x,0) = 0 \quad (15)
\]

\[
c_c(x,0) = 0 \quad (16)
\]

A current response, \( i \), is obtained from the flux of the transferring ion at the membrane/water interface as

\[
i = zAFD_w \left[ \frac{\partial c_w(x,t)}{\partial x} \right]_{x=0} \quad (17)
\]

**Simulation in the Dimensionless Form.** The diffusion problem defined above was solved in a dimensionless form using COMSOL Multiphysics version 3.5a (COMSOL, Inc., Burlington, MA). The example of the finite element simulation is attached. Dimensionless parameters are defined by

\[
C_w(X, \tau) = c_w(x, t)/c_0 \quad (18)
\]

\[
C_i(X, \tau) = c_i(x, t)/c_0 \quad (19)
\]
\[ C_c(X, \tau) = \frac{c_c(x, t)}{c_0} \quad (20) \]
\[ \tau = tvf \quad (21) \]
\[ X = x\sqrt{\frac{vf}{D_w}} \quad (22) \]
\[ L = l_m\sqrt{\frac{vf}{D_w}} \quad (23) \]

where \( f = F/RT \). Diffusion processes (eqs 7–9) are expressed in the respective dimensionless forms as

\[ \frac{\partial C_i(X, \tau)}{\partial \tau} = \frac{2}{i} \left[ \frac{\partial C_i(X, \tau)}{\partial X^2} \right] + K_i' C_i(X, \tau) + K_d C_c(X, \tau) \quad (24) \]
\[ \frac{\partial C_c(X, \tau)}{\partial \tau} = \frac{2}{c} \left[ \frac{\partial C_c(X, \tau)}{\partial X^2} \right] + K_i' C_i(X, \tau) + K_d C_c(X, \tau) \quad (25) \]
\[ \frac{\partial C_w(X, \tau)}{\partial \tau} = \left[ \frac{\partial^2 C_w(X, \tau)}{\partial X^2} \right] \quad (26) \]

with

\[ K_a = \frac{k_a}{vf} \quad (27) \]
\[ K_d = \frac{k_d}{vf} \quad (28) \]
\[ i = \sqrt{\frac{D_i}{D_w}} \quad (29) \]
\[ \epsilon = \sqrt{\frac{D_c}{D_w}} \quad (30) \]

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

\[ \left[ \frac{\partial C_w(X, \tau)}{\partial X} \right]_{X=0} = -\frac{1}{i} \left[ i \begin{pmatrix} C_i(0, \tau) & C_w(0, \tau) \end{pmatrix} \right] \quad (31) \]
\[ \left[ \frac{\partial C_i(X, \tau)}{\partial X} \right]_{X=0} = i \left[ i \begin{pmatrix} C_w(0, \tau) \\ C_i(0, \tau) \end{pmatrix} \right] \quad (32) \]

with
\[ i = \frac{k^0_i}{\sqrt{D_w^i \cdot D_i \cdot f_v}} \]  

(33)

\[ = \exp[zf(E - E_{1/2})] \]  

(34)

\[ E_{1/2} = E_i^0 + \frac{RT}{zF} \ln \sqrt{\frac{D_i}{D_w}} \]  

(35)

Eqs 31 and 32 are equivalent to the expression of a flux boundary condition in COMSOL Multiphysics. The triangle potential wave (eq 4) is given by

\[ q = \exp[zf (E - E_{1/2})] \]  

(36)

with

\[ i = \exp[zf(E_i - E_{1/2})] \]  

(37)

\[ = \exp[zf(E - E_{1/2})] \]  

(38)

A dimensionless current, \( I \), is defined as

\[ I = \left[ \frac{\partial C_w (0, t)}{\partial X} \right]_{X=0} \]  

(39)

With eqs 18 and 22, eq 39 is equivalent to

\[ I = \frac{\sqrt{D_w}}{c_0 \sqrt{f_v}} \left[ \frac{\partial c_w (0, t)}{\partial x} \right]_{x=0} \]  

(40)

The comparison of eq 43 with eq 20 gives

\[ i = (zAFc_0 \sqrt{D_wvf}) I \]  

(41)

REFERENCES

(3) Kim, Y.; Amemiya, S. Anal. Chem. 2008, 80, 6056-6065