# Stripping Analysis of Nanomolar Perchlorate in Drinking Water with Voltammetric Ion-Selective Electrode Based on Thin-Layer Liquid Membrane

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Model. A theoretical model was developed to quantitatively assess ion diffusion in a solid-supported liquid membrane by cyclic voltammetry. The model is analogous to that of a thin mercury film electrode.[1, 2] The geometry of the liquid membrane sandwiched between an aqueous solution and a solid electrode is defined in a linear coordinate, x, vertical to the interfaces. An ion with the charge z_i, i^{z_i}, is initially present only in the aqueous solution. The simple transfer of the ion is defined by

$$i^{z_i} \text{ (aqueous phase)} \rightleftharpoons i^{z_i} \text{ (membrane phase)} \qquad (1)$$
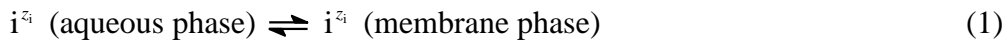
The current based on this ion transfer, i, was numerically calculated by solving the diffusion problem and normalized against the peak current on the forward scan, i_p. The simulated peak current agrees with the value expected for the reversible voltammogram based on semi-infinite linear diffusion as given by[3]

$$i_p = 0.4463 \left(\frac{F^3}{RT} \right) z_i^{3/2} A \sqrt{D_w} c_0 \sqrt{v} \qquad (2)$$

where F is Faraday's constant, A is the interfacial area, D_w and c_0 are the diffusion coefficient and concentration of the ion in the bulk aqueous phase, respectively, and v is the potential sweep rate. The normalized current, i/i_{pa}, was plotted with respect to $|z_i|\Delta\phi$, where $\Delta\phi$ is the overpotential at the liquid membrane/sample solution interface defined as

$$\Delta\phi = \Delta_w^m \phi - \Delta_w^m \phi_i^{0'} \qquad (3)$$

where $\Delta_w^m \phi$ is the Galvani potential difference between the membrane and aqueous phases, and $\Delta_w^m \phi_i^{0'}$ is the formal ion-transfer potential at the membrane/water interface.

Diffusion Problem. A diffusion problem was defined as follows. The diffusion of an analyte ion in the aqueous phase is expressed as

$$\frac{\partial c_w(x,t)}{\partial t} = D_w \left[\frac{\partial^2 c_w(x,t)}{\partial x^2} \right] \qquad (0 < x) \qquad (4)$$

where $c_w(x,t)$ is the local concentration of the transferring ion in the aqueous phase. The diffusion of the ion in the membrane phase is expressed as

$$\frac{\partial c_m(x,t)}{\partial t} = D_m \left[\frac{\partial^2 c_m(x,t)}{\partial x^2} \right] \qquad (-l < x < 0) \qquad (5)$$

where $c_m(x,t)$ is the local concentration of the ion in the membrane phase.

The boundary condition at the membrane/water interface ($x = 0$) is given by

$$D_m \left[\frac{\partial c_m(x,t)}{\partial x} \right]_{x=0} = D_w \left[\frac{\partial c_w(x,t)}{\partial x} \right]_{x=0} = k_f c_w(0,t) - k_b c_m(0,t) \qquad (6)$$

where k_f and k_b are the first-order heterogeneous rate constants for the forward and reverse transfers in eq 1, respectively. The rate constants are given by Butler-Volmer-type relations as[4, 5]

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

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

where k^0 is the standard rate constant, α is the transfer coefficient. In cyclic voltammetry, the potential is swept linearly at a constant rate, v, from the initial potential, $\Delta_w^m \phi_i$, and the sweep direction is reversed at the switching potential, $\Delta_w^m \phi_\lambda$, maintaining the potential sweep rate. This triangle potential wave is expressed as

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

Other boundary conditions are given by

$$D_m \left[\frac{\partial c_m(x,t)}{\partial x} \right]_{x=-l} = 0 \qquad \text{(membrane/solid support interface)} \tag{10}$$

$$\lim_{x \to \infty} c_w(x,0) = c_0 \qquad \text{(simulation limit in the aqueous phase)} \tag{11}$$

Initial conditions are given by

$$c_w(x,0) = c_0 \tag{12}$$

$$c_m(x,0) = 0 \tag{13}$$

The current response based on the ion transfer, i, is obtained from the flux of the transferring ion at the membrane/sample solution interface as

$$i = z_i AFD_w \left[\frac{\partial c_w(x,t)}{\partial x} \right]_{x=0} \tag{14}$$

Simulation in the Dimensionless Form. The diffusion problem defined above was solved in a dimensionless form by using COMSOL Multiphysics version 3.4 (COMSOL, Inc., Burlington, MA), which applies the finite element method. The simulation accuracy of this software package for two-phase diffusion processes was demonstrated previously.[6, 7] Calculation of each CV took <10 s on a workstation equipped with a Xeon 3.0 GHz processor unit and 5.0 GB RAM with Linux. The wave shape on the reverse potential sweep strongly depends on the dimensionless parameter, σ, given by

$$\sigma = \frac{l^2}{D_m} \frac{|z_i| F v}{RT} \tag{15}$$

where l is the membrane thickness, and D_m is the diffusion coefficient of the ion in the membrane phase. This dimensionless parameter is equivalent to the square of the ratio of the membrane thickness with respect to $(D_m RT / |z_i| F v)^{1/2}$, which represents the diffusion distance of the ion in the membrane during a potential cycle. With $\sigma \geq 100$, i.e., $l \geq 10(D_m RT / |z_i| F v)^{1/2}$, the diffusion distance is much smaller than

the membrane thickness so that the nernstian CV is controlled by the semi-infinite linear diffusion of the ion in both phases. With a smaller σ value of 10, the diffusion of the transferred ions in the membrane is hindered by the solid support, thereby resulting in the larger cathodic peak current. The cathodic peak current becomes even larger with $\sigma = 1$, where the membrane serves as a thin layer cell. The cathodic peak based on thin layer behavior is sharper and also shifts toward anodic potentials so that the separation between the anodic and cathodic peak potentials becomes narrower. A further decrease of σ to 0.1 results in the anodic shift of a whole CV while its shape is identical in this regime of thin layer behavior ($\sigma \leq 1$). Overall, a σ value can be determined uniquely from the shape of a reverse wave in the intermediate regime with $1 < \sigma < 100$.

Other dimensionless parameters are defined by

$$C_w(X, \tau) = c_w(x, t)/c_0 \tag{16}$$

$$C_m(X, \tau) = c_m(x, t)/c_0 \tag{17}$$

$$X = x/l \tag{18}$$

$$\tau = D_m t/l^2 \tag{19}$$

Diffusion processes (eqs 4 and 5) are expressed in the respective dimensionless forms as

$$\frac{\partial C_w(X,\tau)}{\partial \tau} = \gamma \left[\frac{\partial^2 C_w(X,\tau)}{\partial X^2} \right] \tag{20}$$

$$\frac{\partial C_m(X,\tau)}{\partial \tau} = \left[\frac{\partial^2 C_m(X,\tau)}{\partial X^2} \right] \tag{21}$$

with

$$\gamma = D_w/D_m \tag{22}$$

The boundary condition at the liquid/liquid interface (eq 6) is expressed using the dimensionless parameters as

$$\gamma \left[\frac{\partial C_w(X,\tau)}{\partial X} \right]_{X=0} = K\theta^{(1-\alpha)} \left[\frac{C_m(0,\tau)}{\theta} - C_w(0,\tau) \right] \tag{23}$$

$$\left[\frac{\partial C_m(X,\tau)}{\partial X} \right]_{X=0} = -\frac{K}{\theta^\alpha} \left[\theta C_w(0,\tau) - C_m(0,\tau) \right] \tag{24}$$

with

$$K = k^0 l/D_w \tag{25}$$

$$\theta = \exp\left[\frac{z_i F(\Delta_w^m \phi - \Delta_w^m \phi_i^{0'})}{RT} \right] \tag{26}$$

$K = 100$ was used for the nernstian ion transfer. The triangle potential wave (eq 9) was given by

$$\theta = \theta_i^{1-(2/\pi)\sin^{-1}\{\sin[\pi\sigma\tau \,/\, 2\ln(\theta_\lambda \,/\, \theta_i)]\}} \theta_\lambda^{(2/\pi)\sin^{-1}\{\sin[\pi\sigma\tau \,/\, 2\ln(\theta_\lambda \,/\, \theta_i)]\}} \tag{27}$$

with

$$\theta_i = \exp\left[\frac{z_i F (\Delta_w^m \phi_i - \Delta_w^m \phi_i^{0'})}{RT}\right] \tag{28}$$

$$\theta_\lambda = \exp\left[\frac{z_i F (\Delta_w^m \phi_\lambda - \Delta_w^m \phi_i^{0'})}{RT}\right] \tag{29}$$

$$\tau_\lambda = \frac{z_i F (\Delta_w^m \phi_\lambda - \Delta_w^m \phi_i)}{RT\sigma} \tag{30}$$

where θ_i is the initial and final potentials in the dimensionless form, θ_λ is the dimensionless switching potential, and τ_λ is the dimensionless switching time. The other boundary conditions and the initial conditions are also given using the dimensionless parameters (see the attached example). The current was normalized with respect to the peak current on the forward scan, i_p, thereby yielding

$$I = \frac{i}{i_p} = \frac{[\P C_w(0, t)/\P X]}{[\P C_w(0, t)/\P X]_p} \tag{31}$$

where $[\P C_w(0, t)/\P X]_p$ is the interfacial gradient of the dimensionless concentration at the anodic peak potential.

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