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Supporting information of

Metal flux through consuming interfaces in ligand mixtures: boundary conditions do not influence the lability and relative contributions of metal species

Zeshi Zhang,*[a] Davide Alemani,[b] Jacques Buffle,[c] Raewyn M. Town[d] and Kevin J. Wilkinson[e]

[a] School of Environmental and Chemical Engineering, Shanghai University, Nanchen Road 333, Shanghai 200444, China
[b] Laboratory for Biomolecular Modeling, Ecole Polytechnique Federale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland
[c] Analytical and Biophysical Environmental Chemistry (CABE), Dept. of Inorganic, Analytical and Applied Chemistry (University of Geneva), Sciences II, 30 quai E. Ansermet, CH-1211 Geneva 4, Switzerland
[d] Institute of Physics and Chemistry, University of Southern Denmark, Campusvej 55, DK5230 Odense , Denmark.
[e] Biophysical Environmental Chemistry Group, Department of Chemistry, University of Montreal, P.O. Box 6128, succursale Centre-ville, Montreal QC, H3C 3J7, Canada

* Corresponding Author:
Zeshi Zhang
School of Environmental and Chemical Engineering, Shanghai University, Nanchen Road 333, Shanghai 200444, China
email: zeshi_zhang@hotmail.com

System with one ligand forming only 1/1 ML complex: mathematical demonstration of the independence of the degree of lability on the boundary condition.

Let us consider a solution containing a metal ion M, and a ligand L in excess with respect to M, which can form a complex ML with equilibrium constant $K = k_a/k_d$ and the association and dissociation rate constants k_a and k_d, respectively. M, ML and L diffuse in solution with their respective diffusion coefficients D_M, D_{ML} and D_L.

For the above diffusion-reaction system, at steady-state, the conservation equations are:

$$D_M \nabla^2_{\text{dim}} [M] + k_d [ML] - k_a [L][M] = 0 \quad (S1)$$

$$D_{ML} \nabla^2_{\text{dim}} [ML] - k_d [ML] + k_a [L][M] = 0 \quad (S2)$$

The dimensional Laplacian operator, ∇_{dim}, depends on the particular geometry considered. For a spherical consuming interface where only M is consumed, the boundary conditions can be written as follows:

at the interface ($r = r_0$):

$$[M] = [M]_0, \qquad \frac{d[ML]}{dr} = 0 \quad (S3)$$

in the bulk solution ($r \geq r_0 + \delta$):

$$[M] = [M]^*, \qquad [ML] = [ML]^* \quad (S4)$$

where superscript * denotes the bulk concentrations. Since L is assumed to be in excess with respect to M, $[L] = [L]^*$ at any distance from the interface.

In order to work with dimensionless parameters we define the normalized diffusion coefficients and concentrations:

$$\varepsilon = \frac{D_{\mathrm{ML}}}{D_{\mathrm{M}}}, \qquad \theta = \frac{[\mathrm{M}]}{[\mathrm{M}]^*}, \qquad \theta^0 = \frac{[\mathrm{M}]_0}{[\mathrm{M}]^*}, \qquad \psi = \frac{[\mathrm{ML}]}{[\mathrm{ML}]^*}, \qquad \rho = \frac{r}{r_0} \tag{S5}$$

Then eqs. S1 and S2 can be rewritten as:

$$\frac{d^2\theta}{d\rho^2} + \frac{2}{\rho}\frac{d\theta}{d\rho} + \frac{k_{\mathrm{a}}[\mathrm{L}]r_0^2}{D_{\mathrm{M}}}\psi - \frac{k_{\mathrm{a}}[\mathrm{L}]r_0^2}{D_{\mathrm{M}}}\theta = 0 \tag{S6}$$

$$\frac{d^2\psi}{d\rho^2} + \frac{2}{\rho}\frac{d\psi}{d\rho} - \frac{k_{\mathrm{d}}r_0^2}{D_{\mathrm{ML}}}\psi + \frac{k_{\mathrm{d}}r_0^2}{D_{\mathrm{ML}}}\theta = 0 \tag{S7}$$

The boundary conditions now read:

$$\text{At } \rho = 1, \qquad \theta = \theta^0 \text{ and } \frac{d\psi}{d\rho} = 0 \tag{S8}$$

$$\text{At } \rho \geq \frac{\delta + r_0}{r_0} = a, \qquad \theta = 1 \text{ and } \psi = 1 \tag{S9}$$

By multiplying the left-hand and right-hand sides of eq. S7 by $\varepsilon K[\mathrm{L}]$ and rearranging with $k_{\mathrm{a}}[\mathrm{L}] = k_{\mathrm{d}}K[\mathrm{L}]$, one obtains:

$$\varepsilon K[\mathrm{L}]\frac{d^2\psi}{d\rho^2} + \varepsilon K[\mathrm{L}]\frac{2}{\rho}\frac{d\psi}{d\rho} - \frac{k_{\mathrm{a}}[\mathrm{L}]r_0^2}{D_{\mathrm{M}}}\psi + \frac{k_{\mathrm{a}}[\mathrm{L}]r_0^2}{D_{\mathrm{M}}}\theta = 0 \tag{S10}$$

By summing eqs. S6 and S10, the kinetic terms cancel out and we get :

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2 \frac{d\left(\theta + \varepsilon K[\mathrm{L}]\psi\right)}{d\rho}\right) = 0 \tag{S11}$$

By integrating eq. S11 with the boundary conditions S8 and S9, we obtain:

$$\theta+\varepsilon K[\mathrm{L}]\psi=\left(\frac{1}{a}-\frac{1}{\rho}\right)\left(\frac{d\theta}{d\rho}\right)_{\rho=1}+1+\varepsilon K[\mathrm{L}] \qquad \text{for } 1\le\rho<a \qquad \text{(S12a)}$$

$$\theta+\varepsilon K[\mathrm{L}]\psi=1+\varepsilon K[\mathrm{L}] \qquad \text{for } \rho\ge a \qquad \text{(S12b)}$$

The normalized concentration profiles of M and ML and the flux equation are found by combining eqs. S6 and S12a to eliminate ψ and introducing the new variable $\omega=\rho\theta$, to yield:

$$\frac{d^2\omega}{d\rho^2}-\frac{k_{\mathrm{a}}[\mathrm{L}]r_0^2(1+\varepsilon K[\mathrm{L}])}{D_{\mathrm{M}}\varepsilon K[\mathrm{L}]}\omega-\frac{k_{\mathrm{a}}[\mathrm{L}]r_0^2}{D_{\mathrm{M}}\varepsilon K[\mathrm{L}]}\left(\frac{d\theta}{d\rho}\right)_{\rho=1}+\frac{k_{\mathrm{a}}[\mathrm{L}]r_0^2}{D_{\mathrm{M}}\varepsilon K[\mathrm{L}]}\left(1+\varepsilon K[\mathrm{L}]+\left(\frac{d\theta}{d\rho}\right)_{\rho=1}\frac{1}{a}\right)\rho=0 \qquad \text{(S13)}$$

In this equation, a combination parameter, λ, appears as a physically meaningful term, i.e. the reaction layer thickness of ML:

$$\lambda=\sqrt{\frac{D_{\mathrm{M}}\varepsilon K[\mathrm{L}]}{k_{\mathrm{a}}[\mathrm{L}](1+\varepsilon K[\mathrm{L}])}} \qquad \text{(S14)}$$

We define:

$$\gamma=r_0\sqrt{\frac{k_{\mathrm{a}}[\mathrm{L}]}{D_{\mathrm{M}}}\left(\frac{1+\varepsilon K[\mathrm{L}]}{\varepsilon K[\mathrm{L}]}\right)}=\frac{r_0}{\lambda} \qquad \text{(S15)}$$

The general solution of eq. S13 is:

$$\theta=\frac{C_1}{\rho}\exp(-\gamma\rho)+\frac{C_2}{\rho}\exp(\gamma\rho)+1+\frac{\left(\frac{d\theta}{d\rho}\right)_{\rho=1}}{1+\varepsilon K[\mathrm{L}]}\left(\frac{1}{a}-\frac{1}{\rho}\right) \qquad \text{(S16)}$$

By using the boundary conditions S8 and S9, and combining eq. S16, we get:

$$C_1 = -\frac{1-\theta^0 + \dfrac{1-a}{(1+\varepsilon K[\mathrm{L}])a}\left(\dfrac{d\theta}{d\rho}\right)_{\rho=1}}{\exp[-\gamma]-\exp[-\gamma(2a-1)]} \quad \text{(S17)}$$

$$C_2 = \frac{1-\theta^0 + \dfrac{1-a}{(1+\varepsilon K[\mathrm{L}])a}\left(\dfrac{d\theta}{d\rho}\right)_{\rho=1}}{\exp[\gamma(2a-1)]-\exp[\gamma]} \quad \text{(S18)}$$

The combination of eqs. S16-S18, yields:

$$J_{\mathrm{t}} = [\mathrm{M}]^* \frac{1-\theta^0}{\dfrac{r_0}{D_{\mathrm{M}}(1+\varepsilon K[\mathrm{L}])}\left(\dfrac{\delta}{r_0+\delta}\right)+\dfrac{r_0\lambda\tanh\left(\dfrac{\delta}{\lambda}\right)}{r_0+\lambda\tanh\left(\dfrac{\delta}{\lambda}\right)}\dfrac{\varepsilon K[\mathrm{L}]}{D_{\mathrm{M}}(1+\varepsilon K[\mathrm{L}])}} \quad \text{(S19)}$$

Due to the continuity of flux, the internalization flux at the consuming interface can be expressed by:

$$J_{\mathrm{int}} = \frac{k_{\mathrm{int}}\{\mathrm{R}\}_{\mathrm{tot}} K_{\mathrm{a}}[\mathrm{M}]_0}{1+K_{\mathrm{a}}[\mathrm{M}]_0} = J_{\mathrm{t}} = \frac{D_{\mathrm{M}}[\mathrm{M}]^*}{r_0}\left(\frac{d\theta}{d\rho}\right)_{\rho=1} \quad \text{(S20)}$$

Now we define:

$$\kappa\theta^0 = \frac{r_0 k_{\mathrm{int}}\{\mathrm{R}\}_{\mathrm{tot}} K_{\mathrm{a}}\theta^0}{D_{\mathrm{M}}(1+K_{\mathrm{a}}[\mathrm{M}]_0)} \quad \text{(S21)}$$

From eqs. S19-21, we get:

$$\kappa\theta^0 = \frac{1-\theta^0}{\dfrac{1}{1+\varepsilon K[\mathrm{L}]}\left(\dfrac{\delta}{r_0+\delta}\right)+\dfrac{\lambda\tanh\left(\dfrac{\delta}{\lambda}\right)}{r_0+\lambda\tanh\left(\dfrac{\delta}{\lambda}\right)}\dfrac{\varepsilon K[\mathrm{L}]}{1+\varepsilon K[\mathrm{L}]}} \quad \text{(S22)}$$

With eq. S12a, we obtain the normalized concentration of ML at the consuming surface:

$$\psi^0 = -\frac{\kappa\theta^0}{\varepsilon K[\mathrm{L}]}\frac{\delta}{r_0+\delta}+1+\frac{1-\theta^0}{\varepsilon K[\mathrm{L}]} \tag{S23}$$

The degree of lability, ξ, of ML in eq. 9 is transformed to be:

$$\xi = \frac{1-\psi^0}{1-\theta^0} \tag{S24}$$

Combining eqs. S22-S24, we arrive at:

$$\xi = \frac{\dfrac{\delta}{r_0+\delta}}{\varepsilon K[\mathrm{L}]\left(\dfrac{1}{1+\varepsilon K[\mathrm{L}]}\left(\dfrac{\delta}{r_0+\delta}\right)+\dfrac{\lambda\tanh\left(\dfrac{\delta}{\lambda}\right)}{r_0+\lambda\tanh\left(\dfrac{\delta}{\lambda}\right)}\dfrac{\varepsilon K[\mathrm{L}]}{1+\varepsilon K[\mathrm{L}]}\right)}-\frac{1}{\varepsilon K[\mathrm{L}]} \tag{S25}$$