Kinetic Mixture Effects in Diffusion Gradients in Thin Films (DGT)

SUPPORTING INFORMATION

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<u>Supplementary information available:</u>

Section 1: Theoretical Framework.
Section 2: Flux and lability degree. (Derivation of eqn. 6 in the text)

1.- Theoretical Framework

Let us consider in solution a mixture of m different metals (${}^i\mathrm{M}$) and h ligands (${}^j\mathrm{L}$) that can react according to the elemental scheme

$$ {}^i\mathrm{M} + {}^j\mathrm{L} \underset{k_{\mathrm{d,ij}}}{\overset{k_{\mathrm{a,ij}}}{\rightleftharpoons}} {}^i\mathrm{M}{}^j\mathrm{L} \qquad i=1..m \qquad j=1..h \qquad \text{(SI-1)} $$

where $k_{\mathrm{a},ij}$ and $k_{\mathrm{d},ij}$ are, respectively, the association and dissociation kinetic constants for the complexation process. The corresponding equilibrium condition for this reaction reads

$$ K_{ij} = \frac{k_{\mathrm{a},ij}}{k_{\mathrm{d},ij}} = \frac{c^*_{{}^i\mathrm{M}{}^j\mathrm{L}}}{c^*_{{}^i\mathrm{M}}\, c^*_{{}^j\mathrm{L}}}, \qquad \text{(SI-2)} $$

where K_{ij} is the equilibrium constant and c_i^* labels the concentration of species i in the bulk solution.

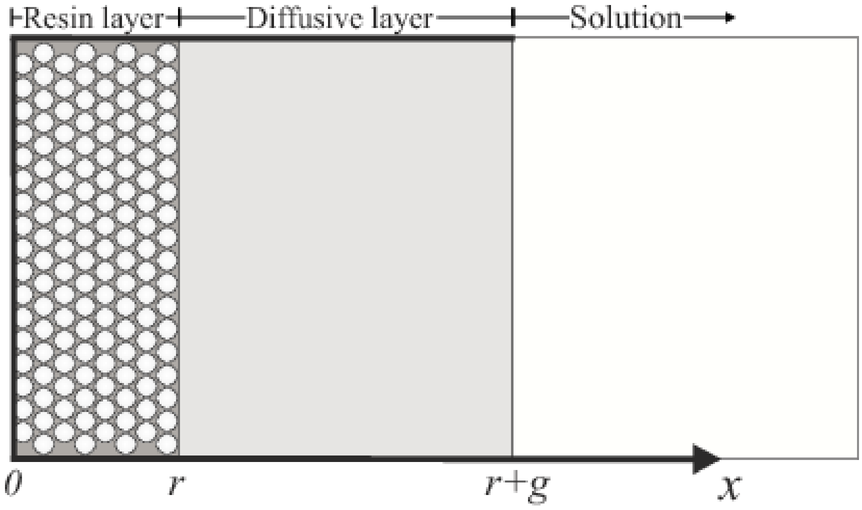

Figure SI-1: Schematic representation of a DGT device.

When a DGT is deployed in the solution, the chemical species diffuse through the diffusive layer (or "gel") towards the binding resin (Figure SI-1). Inside the DGT, each species is affected by diffusion, by reaction with other species or by reaction with the resin. The binding of a metal ${}^{i}\mathrm{M}$ with the resin sites (R) is modeled with the reaction

$$ {}^{i}\mathrm{M}+\mathrm{R} \underset{k_{\mathrm{d},i\mathrm{R}}}{\overset{k_{\mathrm{a},i\mathrm{R}}}{\rightleftharpoons}} {}^{i}\mathrm{MR} \qquad i=1..m \qquad \text{(SI-3)} $$

where $k_{\mathrm{a},i\mathrm{R}}$, $k_{\mathrm{d},i\mathrm{R}}$, and $K_{i\mathrm{R}}=k_{\mathrm{a},i\mathrm{R}}/k_{\mathrm{d},i\mathrm{R}}$ label the corresponding kinetic and stability constants. Only free metal ions bind to the resin sites. Additionally, we assume that complexes also penetrate into the resin gel, but they do not form ternary complexes with the resin. Instead, metal has to dissociate prior to bind to the resin sites[1].

Let us consider the set of complexation reactions (SI-1) and (SI-3). If diffusion is the only relevant transport mechanism, the balance equations for the different species read:

For each metal (${}^{i}\mathrm{M}$), ($i=1..m$) and ligand (${}^{j}\mathrm{L}$), $j=1..h$

$$\frac{\partial c_{{}^{i}\mathrm{M}}}{\partial t} = D^{\mathrm{R}}_{{}^{i}\mathrm{M}} \frac{\partial^2 c_{{}^{i}\mathrm{M}}}{\partial x^2} + \sum_{j=1}^{h}\left(k_{\mathrm{d},ij} c_{{}^{i}\mathrm{M}^{j}\mathrm{L}} - k_{\mathrm{a},ij} c_{{}^{i}\mathrm{M}} c_{{}^{j}\mathrm{L}}\right) + k_{\mathrm{d},i\mathrm{R}} c_{{}^{i}\mathrm{M}\,\mathrm{R}} - k_{\mathrm{a},i\mathrm{R}} c_{{}^{i}\mathrm{M}} c_{\mathrm{R}} \qquad 0<x<r \qquad \text{(SI-4)}$$

$$\frac{\partial c_{{}^{i}\mathrm{M}}}{\partial t} = D_{{}^{i}\mathrm{M}} \frac{\partial^2 c_{{}^{i}\mathrm{M}}}{\partial x^2} + \sum_{j=1}^{h}\left(k_{\mathrm{d},ij} c_{{}^{i}\mathrm{M}^{j}\mathrm{L}} - k_{\mathrm{a},ij} c_{{}^{i}\mathrm{M}} c_{{}^{j}\mathrm{L}}\right) \qquad r<x<r+g \qquad \text{(SI-5)}$$

and for each complex and ligand (${}^{i}\mathrm{M}^{j}\mathrm{L}$), (${}^{j}\mathrm{L}$),

$$\frac{\partial c_{{}^{i}\mathrm{M}^{j}\mathrm{L}}}{\partial t} = D^{\mathrm{R}}_{{}^{i}\mathrm{M}^{j}\mathrm{L}} \frac{\partial^2 c_{{}^{i}\mathrm{M}^{j}\mathrm{L}}}{\partial x^2} + \left(k_{\mathrm{a},ij} c_{{}^{i}\mathrm{M}} c_{{}^{j}\mathrm{L}} - k_{\mathrm{d},ij} c_{{}^{i}\mathrm{M}^{j}\mathrm{L}}\right) \qquad 0<x<r \qquad \text{(SI-6)}$$

$$\frac{\partial c_{{}^{j}\mathrm{L}}}{\partial t} = D^{\mathrm{R}}_{{}^{j}\mathrm{L}} \frac{\partial^2 c_{{}^{j}\mathrm{L}}}{\partial x^2} + \sum_{i=1}^{m}\left(k_{\mathrm{d},ij} c_{{}^{i}\mathrm{M}^{j}\mathrm{L}} - k_{\mathrm{a},ij} c_{{}^{i}\mathrm{M}} c_{{}^{j}\mathrm{L}}\right) \qquad 0<x<r \qquad \text{(SI-7)}$$

$$\frac{\partial c_{{}^{i}\mathrm{M}^{j}\mathrm{L}}}{\partial t} = D_{{}^{i}\mathrm{M}^{j}\mathrm{L}} \frac{\partial^2 c_{{}^{i}\mathrm{M}^{j}\mathrm{L}}}{\partial x^2} + \left(k_{\mathrm{a},ij} c_{{}^{i}\mathrm{M}} c_{{}^{j}\mathrm{L}} - k_{\mathrm{d},ij} c_{{}^{i}\mathrm{M}^{j}\mathrm{L}}\right) \qquad r<x<r+g \qquad \text{(SI-8)}$$

$$\frac{\partial c_{{}^{j}\mathrm{L}}}{\partial t} = D_{{}^{j}\mathrm{L}} \frac{\partial^2 c_{{}^{j}\mathrm{L}}}{\partial x^2} + \sum_{i=1}^{m}\left(k_{\mathrm{d},ij} c_{{}^{i}\mathrm{M}^{j}\mathrm{L}} - k_{\mathrm{a},ij} c_{{}^{i}\mathrm{M}} c_{{}^{j}\mathrm{L}}\right) \qquad r<x<r+g \qquad \text{(SI-9)}$$

Where D_i^{R} and D_i stand for the diffusion coefficients of species *i* in the resin and (diffusive) gel domain respectively. Kinetic constants are zero for those couples (${}^{i}\mathrm{M}$, ${}^{j}\mathrm{L}$) which do not react to form a stable complex (${}^{i}\mathrm{M}^{j}\mathrm{L}$).

Initial and Boundary Conditions

At time $t=0$, that is, at the start of the DGT deployment, the concentration of all species within the device is assumed to be zero, $c_i(x,0)=0$, except for the free binding sites in the resin which initial concentration is $c_{\mathrm{R}}(x,0)=c_{\mathrm{T,R}}$.

For all mobile species, boundary conditions at $x=r+g$ correspond to bulk concentrations:

$$c_i(r+g,t)=c_i^{*} \qquad \text{(SI-10)}$$

In fact, there is evidence that the diffusion domain extends from the gel domain into the adjoining solution. The thickness of this extra layer is called the diffusive boundary layer (DBL)[2]. Here, the DBL is not explicitly considered since, if the difference between the respective diffusion coefficients of M, L and ML in the solution and in the gel layer is negligible, the existence of the DBL can be accounted for by just increasing the effective value of *g*. The diffusion coefficients of metal ions in the filter commonly used to cover the gel layer have been shown to be similar to the values in the gel layer. Therefore this layer is also considered by extending *g*.

At the gel-resin interface (i.e., at $x = r$), the concentrations of mobile species and their fluxes must be continuous (e.g. assuming no electrostatic effect):

$$c_i(r^-,t) = c_i(r^+,t) \qquad \text{(SI-11)}$$

and

$$D_i^{\mathrm{R}} \left.\frac{\partial c_i}{\partial x}\right|_{x=r^-} = D_i \left.\frac{\partial c_i}{\partial x}\right|_{x=r^+} \qquad \text{(SI-12)}$$

Boundary conditions at $x = 0$ stem from non-flux conditions:

$$\left.\frac{\partial c_i}{\partial x}\right|_{x=0} = 0 \qquad \text{(SI-13)}$$

Numerical solution

Discretization

In order to numerically solve the system of equations (SI-4)-(SI-9), the spatial domain is divided into equal segments of length Δx (see Figure SI-2).

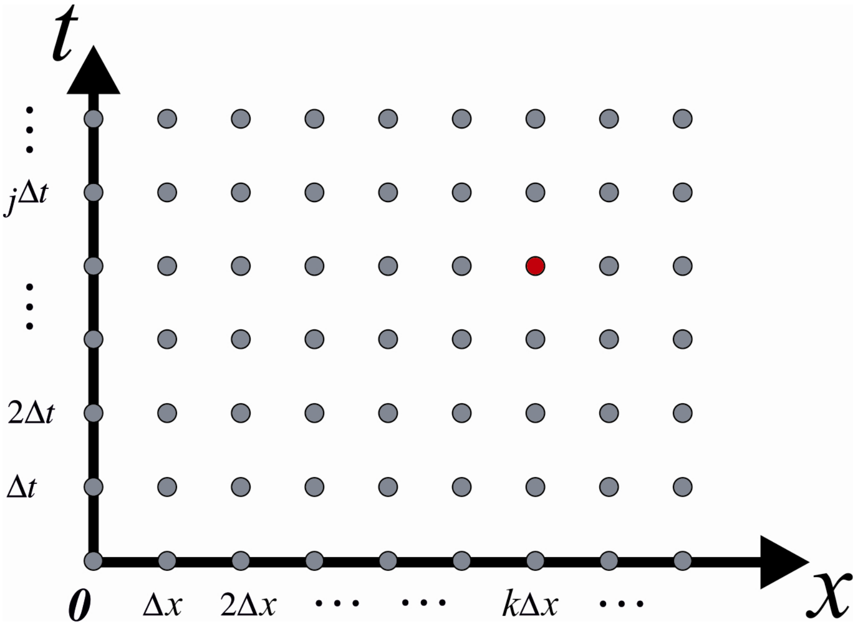

Figure SI-2: Scheme of temporal and spatial discretization.

The partial differential equations are discretized[3] using spatial finite differences and a temporal Inverse-Euler scheme with constant Δt. For instance, the discretized form of equation (SI-4) reads

$$\begin{aligned}\frac{c_{{}^{i}\mathrm{M}}(x,t+\Delta t)-c_{{}^{i}\mathrm{M}}(x,t)}{\Delta t} &= D^{\mathrm{R}}_{{}^{i}\mathrm{M}}\frac{c_{{}^{i}\mathrm{M}}(x+\Delta x,t+\Delta t)-2c_{{}^{i}\mathrm{M}}(x,t+\Delta t)+c_{{}^{i}\mathrm{M}}(x-\Delta x,t+\Delta t)}{\Delta x^2}\\ &+\sum_{j=1}^{h}\left[k_{\mathrm{d},ij}c_{{}^{i}\mathrm{M}{}^{j}\mathrm{L}}(x,t+\Delta t)-k_{\mathrm{a},ij}c_{{}^{i}\mathrm{M}}(x,t+\Delta t)c_{{}^{j}\mathrm{L}}(x,t+\Delta t)\right]\\ &+k_{\mathrm{d},i\mathrm{R}}c_{{}^{i}\mathrm{M}\mathrm{R}}(x,t+\Delta t)-k_{\mathrm{a},i\mathrm{R}}c_{{}^{i}\mathrm{M}}(x,t+\Delta t)c_{\mathrm{R}}(x,t+\Delta t) \qquad \text{for} \quad 0<x<r\end{aligned} \tag{SI-14}$$

Inside this scheme, the initial and boundary conditions in equations (SI-10)-(SI-13) become

$$c_i(r+g,t+\Delta t)=c_i^* \tag{SI-15}$$

$$c_i(r,t+\Delta t)-c_i(r-\Delta x,t+\Delta t)=\frac{D_i}{D_i^{\mathrm{R}}}\left[c_i(r+\Delta x,t+\Delta t)-c_i(r,t+\Delta t)\right] \tag{SI-16}$$

and

$$c_i(\Delta x, t+\Delta t) = c_i(0, t+\Delta t) \qquad \text{(SI-17)}$$

Solution Procedure

The coupled system of non-linear equations obtained by discretization of equations (SI-4) to (SI-9) is solved separately for each species and time. The solution is obtained after iteration and convergence of the concentration of each species at each spatial position considering that the concentration of all other species is known. This procedure is applied iteratively for each species until all the system converges to a solution for each time step. The time is then increased and the first iteration for the next time starts initializing all the unknowns with the values obtained at the previous time. This method allows a extremely large reduction of the computational time in comparison to the CPU time required for the solution of the complete non-linear system using the Newton-Raphson or related methods. More details of this numerical procedure can be found in the SI of [4].

Common parameters used in the numerical simulation are shown in Table 1.

Notice that kinetic and stability constants for the reaction of M with the resin sites reported in Table 1 are assumed to be high enough so that metal concentration practically goes instantaneously to zero in all the spatial positions of the resin domain.

Table 1. Common parameter values for all numerical simulation

Parameter		Value	Units
Resin thickness	r	4×10^{-4}	m
Gel thickness	g	1.13×10^{-3}	m
Association rate constant between M and R	$k_{a,R}$	10^{15}	mol^{-1} m^{3} s^{-1}
Dissociation rate constant between M and R	$k_{d,R}$	10^{-6}	s^{-1}
Diffusion coefficient of M in resin and gel	D_M $D_{M,R}$	6.09×10^{-10}	m^{2} s^{-1}
Diffusion coefficient of L in the resin and gel domains	D_L $D_{L,R}$	4.26×10^{-10} $D_{L,R}=D_L$	m^{2} s^{-1}
Diffusion coefficients of ML in resin and gel	D_{ML} $D_{ML,R}$	4.26×10^{-10} $D_{ML,R}=D_{ML}$	m^{2} s^{-1}
Total concentration of M	$c_{T,M}$	0.01	mol m^{-3}
Total concentration of R	$c_{T,R}$	50	mol m^{-3}
Number of spatial intervals	$(r+g)/\Delta x$	1000	
Temporal interval	Δt	0.1	s

2.- Flux and lability degree. (Derivation of eqn. 6 in the text)

We now work with just one metal (M) and h different ligands. In steady state, all flux passing throw the surface $x=r$ gets bound to the resin. Then, it can be obtained from the sum of metal plus each complex contribution,

$$J = D_{\mathrm{M}} \left.\frac{\mathrm{d}c_{\mathrm{M}}}{\mathrm{d}x}\right|_r + \sum_{j=1}^{h} D_{\mathrm{M}^j\mathrm{L}} \left.\frac{\mathrm{d}c_{\mathrm{M}^j\mathrm{L}}}{\mathrm{d}x}\right|_r \tag{SI-18}$$

On the other hand, by adding all the diffusion equations given in (SI-4)-(SI-9) for $r<x<r+g$, we obtain

$$\frac{d^2 c_{\mathrm{M}}}{\mathrm{d}x}\left(D_{\mathrm{M}} c_{\mathrm{M}} + \sum_{j=1}^{h} D_{\mathrm{M}^j\mathrm{L}} c_{\mathrm{M}^j\mathrm{L}} \right) = 0, \tag{SI-19}$$

or

$$D_{\mathrm{M}} c_{\mathrm{M}} + \sum_{j=1}^{h} D_{\mathrm{M}{}^{j}\mathrm{L}} c_{\mathrm{M}{}^{j}\mathrm{L}} = Ax + B \quad \text{for} \quad r < x < r + g. \qquad \text{(SI-20)}$$

Solving this system alongside with boundary conditions (SI-10)-(SI-12) and applying eqn. (SI-18) the total metal flux can be rewritten[5-8] as,

$$J = \frac{D_{\mathrm{M}} c_{\mathrm{M}}^{*}}{g} + \sum_{j=1}^{h} \left[\frac{D_{\mathrm{M}{}^{j}\mathrm{L}} c_{\mathrm{M}{}^{j}\mathrm{L}}^{*}}{g} \left(1 - \frac{c_{\mathrm{M}{}^{j}\mathrm{L}}^{r}}{c_{\mathrm{M}{}^{j}\mathrm{L}}^{*}} \right) \right]. \qquad \text{(SI-21)}$$

which coincides with eqn. (6) in the running text.

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