

Supporting information for Diffusion and Partitioning of Cations in an Agarose Hydrogel

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1. Diffusion Theory. When a substance moves at constant temperature and pressure, the work that is performed can be described with respect to the opposing force, which is considered a thermodynamic force^{1,2}:

$$F = - \left(\frac{\partial \mu_i}{\partial x} \right)_{T,P} \quad (S1)$$

where the chemical potential changes in the x direction. The flux of material, J , is proportional to this force and can be described by³:

$$J = -D \frac{c}{RT} \left(\frac{\partial \mu_i}{\partial x} \right) \quad (S2)$$

where D is the diffusion coefficient, R is the universal gas constant, T is the temperature and c is the concentration. Flux is a time-independent factor in this equation. The chemical potential of compound i, μ_i , is dependent upon the temperature (T), pressure (P), compound activity (a_i) and long range electrostatic interactions:

$$\mu_i = \mu_i^0 + V_i(p - p^0) + RT \ln a_i - S_i(T - T^0) + \mu_{i,el} \quad (S3)$$

where $\mu_{i,el}$ accounts for electrostatic interactions. When changes in pressure and temperature are negligible, Equation S3 becomes⁴:

$$\mu_i = \mu_i^0 + RT \ln a_i + \mu_{i,el} \quad (S4)$$

In dilute solutions, the activity can be replaced by the concentration. Combination of Equations S2 and S4 gives:

$$J = -D \frac{c}{RT} \left(\frac{RT}{c} \frac{\partial c}{\partial x} + \frac{\partial \mu_{el}}{\partial x} \right) \quad (S5)$$

which is Fick's first law. In Equation S5, there are contributions from a concentration gradient and electrostatic charges. If no charges are present, then $\partial \mu_{el} / \partial x = 0$ approaches zero and the equation can be simplified to:

$$J = -D \frac{\partial c}{\partial x} \quad (S6)$$

which is the form of the Equation that is generally used in high ionic strength solutions.

2. Diffusive flux of an ion obtained using the Diffusion Equilibration Technique (DET)⁵. In diffusion cell, the steady-state flux of a solute passing through an agarose hydrogel, using Equation 6, can be given by:

$$J = D_g^m \frac{dc_g}{dx} \quad (S7)$$

where D_g^m ($\text{cm}^2 \text{ s}^{-1}$) is the mutual diffusion coefficient of the solute and c_g is its concentration in the hydrogel. Equation S7 can be rewritten as:

$$J = D_g^m \frac{(c_g^s - c_g^r)}{\ell} \quad (S8)$$

where ℓ is the gel thickness and c_g^s and c_g^r are the concentrations of the solute at the gel/source and gel/receiving solution interfaces, respectively. For an ionic solute, the electrostatic partition coefficient at both interfaces of the hydrogel, i.e. the total concentration of the ion in the gel with respect to that in the solution is given by:

$$\Pi = \frac{c_g^s}{c_w^s} = \frac{c_g^r}{c_w^r} \quad (S9)$$

where c_w^s and c_w^r are concentrations of the ion in the source and receiving solutions, respectively. If the diffusion boundary layer thicknesses at both interfaces are negligible then the flux can be obtained by combining Equations S8 and S9:

$$J = \frac{\Pi D_g^m (c_w^s - c_w^r)}{\ell} \quad (S10)$$

Since the flux ($\text{mol cm}^{-2} \text{ min}^{-1}$) is simply the change in the number of moles of solute over time (dN/dt) for a given surface of hydrogel, A , it is possible to determine the mutual diffusion coefficient of the ion in the gel from the measured change in concentration (N/V) of a given volume, V , of receptor solution:

$$\frac{dc}{dt} = \frac{A \Pi D_g^m (c_w^s - c_w^r)}{V \ell} \quad (S11)$$

Typically, ΠD_g^m is obtained from the slope of the initial (linear) increase of concentration in a receiving solution (initial concentration=0, Figure S1).

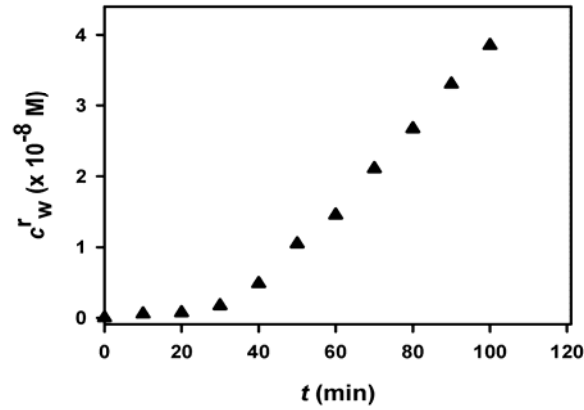


Figure S1. Cd ion concentration in receiving compartment of a DET as a function of time. $c_w^r = 10^{-5}$ M, $I=10^{-4}$ M, pH=6, Cd measured by GF-AAS. The slope calculated here was 6×10^{-10} M min⁻¹ ($A=6.84$ cm², $\ell=0.095$ cm, $V=100$ cm³).

3. Partition coefficient. It must be noted that the partitioning of Cd in the gel does not simply result from electrostatic interactions. In fact, the overall partition coefficient (Φ) in the hydrogel results from steric (θ), electrostatic (Π) and chemical (α) interactions such that $\Phi = \theta \Pi \alpha$.⁵ In this paper, we have assumed that the contribution of bound Cd (θ , α) to the overall diffusive flux can be neglected. In fact, this observation is borne out by both the transient current measurements (Fig. S2 below) and by the chemical extraction measurements (Fig. 4 in the paper).

4. Donnan Potential. Uncompensated immobile charges in the agarose gel will lead to the development of a Donnan potential. In this case, the negative potential of the gel will result in an increased concentration of cations in the gel with respect to the bulk medium. The Donnan potential for a symmetrical z - z electrolyte is given by:

$$\psi_D = \frac{RT}{zF} \arcsin\left(\frac{z_g \rho}{2zc}\right) \quad (\text{S12})$$

where z represents the charge number of the electrolytes, z_g is the charge number of the functional groups in the gel, ρ the volume charge density of the gel and c is the bulk electrolyte concentration in the medium. Other expressions have been derived for more complex electrolyte mixtures.⁶

For a more complex mixture of 2-1 and 1-1 electrolytes (e.g., $\text{Cd}(\text{NO}_3)_2 + \text{NaNO}_3$), Ohshima and Kondo derived the following set of expressions:

$$-\frac{1-\eta}{2}e^{-y} - \frac{\eta}{3}e^{-2y} + \frac{3-\eta}{6}e^y - \frac{\rho}{2c_1 + 3c_2} = 0 \quad (\text{S13})$$

$$y = \frac{F\psi_D}{RT} \quad (\text{S14})$$

$$\eta = \frac{3c_2}{c_1 + 3c_2} \quad (\text{S15})$$

where c_1 and c_2 are the concentrations of 1:1 and 2:1 electrolytes, respectively. The functional groups in the agarose hydrogel are normally carboxylate groups and other functional groups such as sulfonate, which have a negative value for z . The protonation of the functional group sites needs to be considered for pH values in the range of the relevant $\text{p}K_a$ of the gel.

5. Does bound Cd contribute to Cd diffusion? Transient voltammetry was performed to reveal whether Cd bound to the gel phase could contribute to the Cd flux at the electrode surface. When the reduction current, I , is plotted as a function of time, the area

under the curve corresponds to the amount of Cd that is reduced at the electrode surface. The hatched areas in Figure S2 represent the transient responses for the gel and for water prior to the attainment of the steady-state current (symbolized by the horizontal line). As shown in Fig. S2, an upward shift in the (negative) steady-state current was observed for measurements performed in the gel. Nonetheless, the nature of the transient response was similar in solution and in the gel with the apparent attainment of steady-state conditions after a few seconds. The combination of an increased steady-state current and a similar transient response strongly suggests that the voltammetric technique was only measuring diffusion limited Cd within the pores of hydrogel and not Cd bound to the hydrogel ⁷. These curves are consistent with results from the paper (Fig. 3b) showing that the electrostatic partition coefficient was nearly identical to the overall partition coefficient.

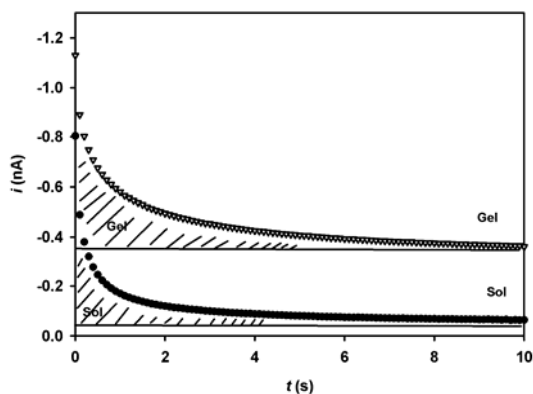


Figure S2. Current transient for Cd ion reduction at $E_d = -0.8$ V in the gel and in solution, $c_{Cd}=10^{-5}$ M, $I= 5 \times 10^{-4}$ M, r_0 (diameter of microelectrode)= 25 μ m.

6. Structure of Rhodamine 6G

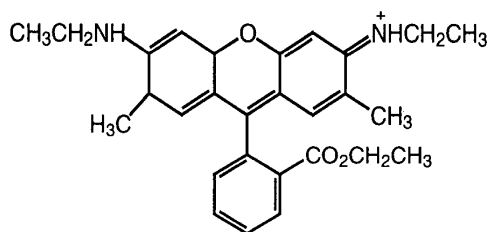


Figure S3. Structure of rhodamine 6G

Bibliography

1. Atkins, P. W., *Physical chemistry*; W. H. Freeman: San Francisco, **1978**.
2. Crank, J., *The mathematics of diffusion*. 2nd ed; Clarendon Press: Oxford, **1975**.
3. Mattisson, C.; Roger, P.; Jonsson, B.; Axelsson, A.; Zacchi, G. *J. Chromatogr. B* **2000**, *743*, 151-167.
4. Wesselingh, J. A., *Mass Transfer in Multicomponent Mixtures*; Delf University Press: Delf, **2000**.
5. Fatin-Rouge, N.; Milon, A.; Buffle, J.; Goulet, R. R.; Tessier, A. *J. Phys. Chem. B* **2003**, *107*, 12126-12137.
6. Ohshima, H.; Kondo, T. *Biophys. Chem.* **1990**, *38*, 117-122.
7. Kalis, E. J. J.; Davis, T. A.; Town, R. M.; Van Leeuwen, H. P. *Environ. Sci. Technol.* **2009**, *43*, 1091-1096.