Origins of concentration gradients for diffusiophoresis

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Supplementary Information

Scaling Analysis in Electrolyte Diffusiophoresis:

Defining Notations: 1 => solute, 2 => solvent; N_1 => no. of solute moles and N_2 => no. of solvent moles

$$U = \left(\frac{\epsilon KT}{\eta Ze}\beta\zeta_p\right)\frac{\nabla C_1}{C_1} = \frac{\dfrac{\nabla C_1}{C_1}}{\dfrac{1}{\dfrac{\epsilon KT}{\eta Ze}\beta\zeta_p}} = \gamma \, \nabla(logC_1)$$

Diffusiophoretic velocity (U):

Assumptions: 1. Very dilute system in terms of salt (N_1 is negligible), 2. Ideal solution (activity co-eff., γ_1 & $\gamma_2 \sim 1.0$), 3. Constant temperature and pressure, 4. N_2 is invariant over space (1-dimensional), 5. z-directional or mono directional diffusion of solute.

Chemical potential of solute: $\mu_1 = \mu_1^0 + RT\log(\gamma_1 C_1)$

Applying grad. on both sides of the above equation-

$\nabla\mu_1 = \nabla\mu_1^0 + RT\nabla(log\gamma_1 + logC_1)$

$\nabla\mu_1^0 = 0$; standard (reference) chemical potential does not vary over space

$\nabla \, log\gamma_1 = 0$; ideal solution

The above equation simplifies to- $\nabla\mu_1 = RT\nabla \, logC_1$

Now combining the diffusiophoretic velocity equation-

$$U = \frac{\gamma}{RT}\nabla\mu_1 \quad \textbf{(1)}$$

Therefore, diffusiophoresis is driven by change in chemical potential with resistance equivalent to $\frac{RT}{\gamma}$

Total Gibbs free energy of the system: $G = \mu_1 N_1 + \mu_2 N_2$

Applying grad. on both sides of the above equation-

$$\nabla G = \mu_1\nabla N_1 + N_1\nabla\mu_1 + \mu_2\nabla N_2 + N_2\nabla\mu_2$$

$\mu_2\nabla N_2 \approx 0$; N_2 is space invariant in dilute solution

$N_2\nabla\mu_2 \approx 0$; $\nabla\mu_2 \approx 0$ as $\nabla\mu_2 = \nabla\mu_2^0 + RT\nabla(log\gamma_2 + logC_2)$ ...where $\nabla\mu_2^0 = 0$, $\nabla log\gamma_2 = 0$ and $\nabla logC_2 \approx 0$, because C_2 is almost invariant over space

$N_1\nabla\mu_1 \approx 0$; since for a very dilute system N_1 becomes negligible

Therefore, simplification of the above equation in the limit of "extreme dilution"-

$$\nabla G = \mu_1\nabla N_1$$

$$\Rightarrow \mu_1 = \frac{\nabla G}{\nabla N_1}$$

$$\Rightarrow \nabla\mu_1 = \nabla(\frac{\nabla G}{\nabla N_1})$$

$$\Rightarrow \nabla\mu_1 = \nabla(\frac{\frac{\partial G}{\partial z}}{\partial N_1})$$

$$\Rightarrow \nabla\mu_1 = \nabla(\frac{\frac{\partial G}{\partial z}}{\partial N_1})$$

From Equation (1), substituting $\nabla\mu_1$, we can write-

$$U = \frac{\gamma}{RT}\nabla\mu_1 \underset{=RT}{=}\frac{\gamma}{RT}\nabla\left(\frac{\partial G}{\partial N_1}\right) = \gamma\nabla\left(\frac{\partial G}{\partial(N_1 RT)}\right) = \gamma\nabla\left(\frac{\partial G/V}{\partial(N_1 RT/V)}\right) = \gamma\nabla\left(\frac{\partial\bar{G}}{\partial\pi}\right)$$

Therefore, for a dilute system (with volume V) -

$$U = \gamma \lim_{N1 \to 0} \nabla\left(\frac{\partial \overline{G}}{\partial \pi}\right) \qquad \textbf{(2)}$$

$\overline{G}$ is the volume specific Gibbs free energy (J/m³), π is the osmotic pressure imparted by solute (Pa) and γ is "diffusiophoretic diffusivity"

Equation (2) can be approximated as follows for a dilute system-

$$U \approx \gamma \frac{\left(\frac{\Delta \overline{G}}{\Delta \pi}\right)}{L} \qquad \textbf{(3)}$$

L is characteristic length scale of the system. For reverse osmosis membrane systems processing 10 mM NaCl feed with system volume 1 L-

$N_1 = 0.01$

$N_2 = 55.56$

Mole fractions, $x_1 = 0.00018$ and $x_2 = 0.00082$

$\Delta G_{mix} = (N_1 + N_2)\, RT\, (x_1 \log (x_1) + x_2 \log (x_2))$

$$\frac{\Delta \overline{G}_{mix}}{\Delta \pi} = \frac{(N_1 + N_2)RT\,(x1\,\log\,(x1)\ +\ x2\,\log\,(x2))/V}{N_1 RT/V} \approx -10$$

For U ~ O(10⁻⁶) m/s and $\gamma \sim O(10^{-10})$ m²/s, L ~ 1 mm which is reasonable as of the order of concentration boundary layer.

Diffusiophoretic transport can be significant across or along a surface, particularly if the surface is porous or semipermeable and obstructs free diffusion. In such a system, analogous to diffusion co-efficient, we can define a "diffusiophoretic co-efficient" as $\sigma_p = \lim_{N_{solute} \to 0} \nabla(\partial \overline{G}/\partial \pi)$ for dilute solutions ($N_{solute} \to 0$), where π signifies the osmotic pressure exerted by solutes. This terminology resembles Kedem-Katchalsky reflection co-efficient $\sigma_m = (\partial P/\partial \pi)_{J_v = 0}$ which quantifies the intrinsic semipermeability of membranes[1]. Diffusiophoretic velocity (U$_{dp}$) at lower solute concentrations, in terms of salt gradients generated electrophoresis, can be expressed analogous to Fickian diffusive flux as follows-

$$U_{dp} = \left(\frac{\in_m KT}{\eta Ze}\beta\, \zeta_p \lim_{N_{solute} \to 0} \nabla\left(\frac{\partial \overline{G}}{\partial \pi}\right)\right) = \gamma\, \sigma_p \qquad \textbf{(4)}$$

Where, γ has similar units and the same order of magnitude values as diffusion coefficient of salts. The above expression elucidates that diffusiophoresis can be exacerbated in cases where spatial variation of volumetric Gibbs free energy ($\bar{G}$) is higher, such as in concentration boundary layers and deposited particulate layers such as those on salt rejecting membranes, in protein transport through micropores, and in deposited gel layers on ultrafiltration membranes. If applied pressure is just able to resist osmotic pressure of solute on membrane, transport across membrane ceases and σ_m *becomes* 1 which is the case of ideal semi-permeable membrane. Similarly, diffusiophoresis ceases only when volumetric Gibbs free energy does not change spatially, ratio of local volumetric Gibbs free energy to osmotic pressure changes remains constant over space or local osmotic pressure change becomes exceedingly dominant over volumetric Gibbs free energy change. In all these cases, σ_p *becomes* 0.

References

1   M. Kargol and a. Kargol, *Biophys. Chem.*, 2003, **103**, 117–127.