IV. Transport Phenomena

Lecture 22: Transport in Bulk Electrolytes

MIT Student

1 Nernst-Planck Equations

The continuity equation for a species i is an expression of conservation of that species under conditions where the concentration can be assumed to be a continuous field. The continuity equation can be expressed in vectorial form as

$$\frac{\mathrm{Dc_i}}{\mathrm{Dt}} = -\nabla\cdot\ \mathbf{F}_\mathrm{i}$$

For a dilute solute, that is, for a solute whose concentration is sufficiently small that the particles diffuse independently and are not coupled by the motion of the surrounding fluid (or any other interaction), the flux $\mathbf{F}_\mathrm{i}$ is given by Fick's law as $\mathbf{F_i} = -\mathrm{D_i}\nabla\mathrm{c_i}$. However, in the case of a charged solute subject to an electric field, the solute flux has a contribution of the form $\mathbf{F}_{\mathrm{i,E}} = \mathrm{c_i M_i}(\mathrm{z_i e}\mathbf{E})$, where $\mathrm{M_i}$ is the mobility of the solute in solution. Using the Einstein relation between the mobility and the diffusivity, and writing the electric field in terms of the scalar potential, the total flux is

$$\mathbf{F_i} = -\mathrm{D_i}\left(\nabla\mathrm{c_i} - \mathrm{c_i}\frac{\mathrm{ez_i}}{\mathrm{k_B T}}\nabla\phi\right)$$

The charge density in the fluid in terms of the concentrations is

$$\rho = \sum_i \mathrm{z_i e c_i}$$

2 Electrical Conduction and Diffusion Current

Consider a binary electrolyte with a cation of charge $\mathrm{z_+e}$ and concentration $\mathrm{c_+}$, and an anion of charge $\mathrm{z_-e}$ and concentration $\mathrm{c_-}$. Under the assumption

of electroneutrality,

$$\begin{aligned} \rho &= 0 \\ e\sum_i z_i c_i &= 0 \\ z_+ c_+ &= z_- c_- \end{aligned}$$

We can thus define

$$c_\pm = z_+ c_+ = z_- c_-$$

After non-dimensionalizing the potential by $\frac{k_B T}{e}$, the two Nernst-Planck equations are

$$\begin{aligned} \frac{\partial c_+}{\partial t} &= D_+ \left(\nabla^2 c_+ + z_+ \nabla \cdot (c_+ \nabla \psi)\right) \\ \frac{\partial c_-}{\partial t} &= D_- \left(\nabla^2 c_- - z_- \nabla \cdot (c_- \nabla \psi)\right) \end{aligned}$$

Applying electroneutrality

$$0 = \frac{\partial \rho}{\partial t} = \frac{\partial}{\partial t}\left(z + e c_+ - z_- e c_-\right) = e(D_+ - D_-)\nabla^2 c_\pm + e\left(D_+ z_+ + D_- z_-\right)\nabla \cdot (c_\pm \nabla \psi)$$

Which, from conservation of charge $\frac{\partial \rho}{\partial t} = -\nabla \cdot \mathbf{J}$ implies a current density

$$-\mathbf{J} = e(D_+ - D_-)\nabla c_\pm + e\left(D_+ z_+ + D_- z_-\right)(c_\pm \nabla \psi)$$

and a conductivity

$$\sigma = \frac{e^2}{k_B T}\left(z_+ D_+ + z_- D_-\right) c_\pm$$

This is a generalization of Ohm's law since the current density is linear in the (non-constant) field $\mathbf{E} = \nabla \phi$.

3 Ambipolar Diffusion

Analogous to the previous section where the two Nernst-Planck equations were essentially subtracted, now the two equations are added to yield

$$2\frac{\partial c_\pm}{\partial t} = \frac{\partial}{\partial t}\left(z_+ c_+ + z_- c_-\right) = e(D_+ + D_-)\nabla^2 c_\pm + \left(z_+ D_+ - z_- D_-\right)\nabla \cdot (c_\pm \nabla \psi)$$

Solving for $\nabla\psi$ from the equation for charge conservation yields

$$\nabla \cdot (c_\pm \nabla\psi) = \frac{\mathrm{D_+ - D_-}}{\mathrm{z_+D_+ + z_-D_-}} \nabla^2 \mathrm{c_\pm}$$

Replacing this term in the previous equation gives the ambipolar diffusion equation

$$\frac{\partial \mathrm{c_\pm}}{\partial \mathrm{t}} = \mathcal{D}\nabla^2 \mathrm{c_\pm}$$

where the effective diffusivity is

$$\mathcal{D} = \frac{\mathrm{D_+D_-(z_+ + z_-)}}{\mathrm{z_+D_+ + z_-D_-}}$$

The ambipolar diffusion equation expresses the coupling of the positive and negative species under the electroneutrality assumption. That is, the expression shows that since the solution is electrically neutral, the two species must diffuse together, and in a way that is dependent on their individual diffusivities and relative concentrations. This analysis is effective at describing bulk solutions, but near charged surfaces the electroneutrality assumption breaks down, and the equation is no longer valid.

Expressed in terms of the mobilities, the ambipolar diffusion constant is

$$\mathcal{D} = \frac{\mathrm{M_-D_+ + M_+D_-}}{\mathrm{M_+ + M_-}}$$

The ambipolar diffusion constant is a weighted sum of the regular diffusion constants, where the weight is the mobility of the other species. The diffusion is dominated by the smaller mobility. As an analogy, consider an equal number of teachers and small children traversing a crowded room. Even though the child has the tendency to move much faster than his accompanying teachers, he is limited in the extent of his mobility by the teacher's speed and position, which dominates the overall transport. Similarly, the teachers always move so as to maintain a constant student-teacher ratio (electroneutrality).

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