

Lecture 16

Solute Transport Across Partially Permeable Membranes

In this lecture, we would like to understand transport of the solute, which can be macro-molecules or charged nanoparticles, across a partially permeable membrane. As shown in 16.1, consider a membrane separating left and right reservoirs with solute concentrations C_1 and C_2 , respectively. Because there is a concentration difference $\Delta C = C_2 - C_1$, the chemical potential difference will induce mass transfer across the membrane. Before starting to analyze the system, the first consideration is about the time scale. Clearly, the membrane is not infinitely thin, so there would be a concentration distribution within the membrane, together with the fact that upon solute transport, the right and left reservoir concentrations will be functions of time. Do we need to solve time-dependent mass transfer equation in the membrane? What assumptions or prerequisites are required to simplify the problem?

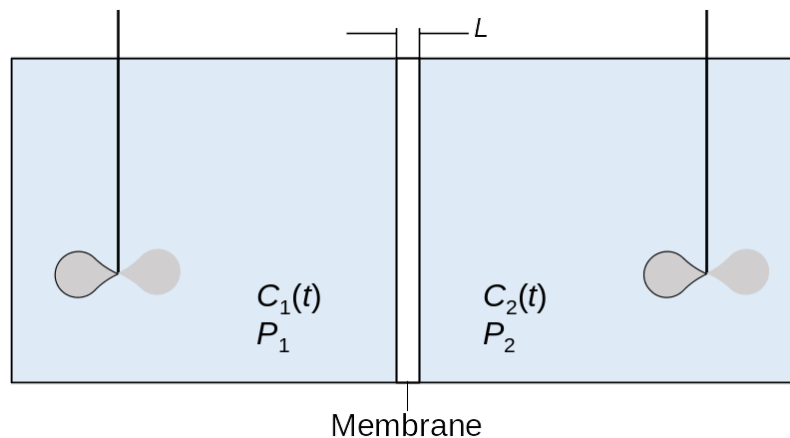


Figure 16.1: A typical membrane system in which a semi-permeable membrane separating two reservoirs, with the solute concentrations of C_1 and C_2 as a function of time assuming well mixing.

First we consider a system in which the solute transport is completely driven by chemical potential, i.e., concentration difference ΔC , and the fluid flow across the membrane is negligible. Here there are two time scales, including that for the diffusion across the membrane $\tau_D = L^2/D$, and that for the concentration change in the reservoir $\tau_V = V\Delta C/NA$, where L is the membrane thickness, A is the membrane area, V is the reservoir volume, N is the solute flux, and D is the diffusivity. Since only diffusion is considered here $N = -(D\Delta C/L)\omega$, where ω is the solute permeability across the membrane (will be further discussed in details later), τ_V is therefore given by:

$$\tau_V = \frac{VL}{DA\omega} \quad (16.1)$$

At a pseudo steady state, the time dependence for the concentration profile in the membrane becomes negligible. The most important requirement that the approximation can hold is that the rate at which the membrane concentration profile can adjust is significantly faster than that at which the external concentration change, or in other words $\tau_V \gg \tau_L$, or:

$$\frac{AL\omega}{V} \ll 1 \quad (16.2)$$

In that case, one can also solve the concentrations of the two reservoirs following:

$$\begin{aligned} V\frac{dC_1}{dt} &= -NA = \left[\frac{D(C_1 - C_2)}{L} \right] \omega A \\ V\frac{dC_2}{dt} &= +NA = - \left[\frac{D(C_1 - C_2)}{L} \right] \omega A \end{aligned} \quad (16.3)$$

With the initial conditions of $C_1(t = 0) = C_{1,0}$ and $C_2(t = 0) = C_{2,0}$, the above ODEIVP can be easily solved analytically or numerically.

16.1 Pressure and concentration driven solute/solvent system

When two solutions interact with each other via a permeable membrane (interface), transport occurs through a complex interplay between solute and solvent. Transport can be driven by pressure, concentration difference and electrical forces, while both solute and solvent can carry each other across the membrane. While such systems are in general complex, a considerable simplification can be achieved for low solute concentration, where solute-solvent transport interactions become linear.

Historically, pressure and concentration driven solute and solvent transport were known well before electric-field originated transport. Therefore, here we can start with concentration-driven solute/solvent system. While pure solute transport due to concentration difference can be solved by diffusion equations, pure solvent transport is subtler and can be explained in the context of osmosis. For low solute concentrations, the osmotic pressure can be found by the van't Hoff law [1],

$$\Delta\Pi = k_B T \Delta c \quad (16.4)$$

where Δc indicates the concentration difference between the two reservoirs separated by the membrane. The van't Hoff law well describes the case of ideal solute-impermeable membrane, where only the solvent can be driven by the concentration gradient (osmotic pressure). However, when the membrane is partially permeable to the solute, solute can also diffuse across the membrane. On the other hand, since each solute molecule/ion can have a shell that contains solvent molecules, the solvent flux would be reduced. We therefore define a dimensionless rejection factor σ , such that the effective osmotic pressure difference becomes $\Delta\Pi_{\text{eff}} = \sigma k_B T \Delta c$. By assuming the solvent flow within the membrane is Hagen-Poiseuille-like, the solute flux, N , and the area-averaged solvent flow rate (or velocity) $\langle v \rangle$, across the membrane can be described as follows:

$$\begin{aligned} \langle v \rangle &= -\mathcal{L}_{\text{hyd}}(\Delta p - \sigma k_B T \Delta c) \\ N &= -L_D \omega (\Delta c + c \langle v \rangle) \end{aligned} \quad (16.5)$$

where c is the solute concentration, p is the pressure and Δ corresponds to the difference from left to right ($+x$ direction) reservoir, \mathcal{L}_{hyd} is the solvent permeance through the membrane, defined as $\mathcal{L}_{\text{hyd}} = \kappa/(\eta L)$, where η is the solvent's dynamic viscosity, L is the membrane thickness and κ is the porous media permeability for the membrane (in units of Darcy or length square); L_D is the solute permeance, defined as $L_D = D/L$, where D is the diffusivity of the solute. Here, we also define another dimensionless factor ω corresponding to the solute permeability coefficient across the membrane. The equations above are also known as the Kedem-Katchalsky relations [2]. Here, the solvent flow is proportional to the effective pressure across the membrane, which is a sum of the externally applied pressure (Δp) and the effective osmotic pressure ($-\sigma k_B T \Delta c$).

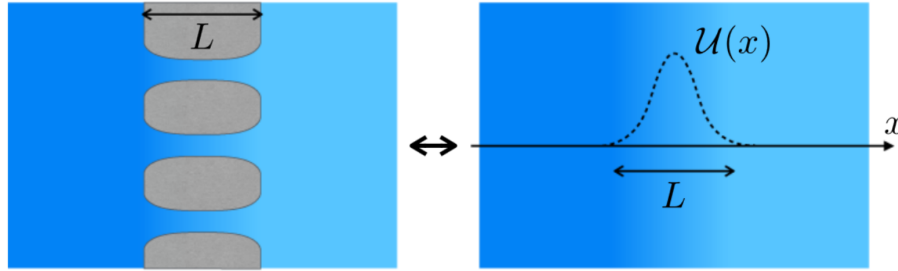


Figure 16.2: Geometry of the membrane (interface) separating two solutions with different solute concentrations. The membrane can be mathematically described as a potential acting on the solute transport. [3]

Now we would like to know the relation between the solute rejection factor σ and the permeability ω . First, we notice that when the solute rejection factor $\sigma = 0$, meaning the existence of membrane does not hinder solute diffusion, the solute flux should reduce to $N = -L_D \Delta c$ or $\omega = 1$. In order to further understand the two empirical parameters σ and ω , we can imagine that the membrane offers an energy barrier to the solute transport (see 16.2). One can therefore introduce an hypothetic potential distribution within the membrane $U(x)$, where x is the coordinate within the membrane with the origin located at the

film center, as shown in Fig. 16.2. Following the spirit of the Nernst-Planck equation discussed in Lecture 14, we can describe the solute transport equation within the membrane following:

$$\frac{\partial c}{\partial t} = 0 = -\frac{\partial N}{\partial x} = -\frac{\partial}{\partial x}(-D\frac{\partial c}{\partial x} + uc\left(-\frac{\partial U}{\partial x}\right) + cv_f) \quad (16.6)$$

where v_f is the fluid velocity as a function of x and u is the solute mobility expressed by the Einstein relation $u = D/(k_B T)$. If we assume the convective contribution has negligible effect on the concentration profile, i.e., low Peclet number in membrane, at steady state the flux N appears to be a constant, such that the concentration profile within the membrane, $c(x)$ can be solved explicitly given by (for details, see Ref. [4])

$$c(x) = -\Delta c \exp\left(-\frac{U(x)}{k_B T}\right) \times \frac{\int_x^{L/2} \exp\left(-\frac{U(\tilde{x})}{k_B T}\right) d\tilde{x}}{\int_{-L/2}^{L/2} \exp\left(-\frac{U(\tilde{x})}{k_B T}\right) d\tilde{x}} \quad (16.7)$$

It will require the potential profile within the membrane $U(x)$, to analytically solve $c(x)$. In order to find the next relation, we consider the force balance acting on solute within the membrane, based on the Stoke equation, the force vector of the membrane potential acting on solute is given by $-\nabla U$, so the force acting on solute per unit volume is given by $-c(x)\partial U/\partial x$. Together with the Stoke equation (at low Reynold number), the force balance within the membrane is given by:

$$-\frac{\partial p}{\partial x} - c(x)\frac{\partial U}{\partial x} + \eta\nabla^2 v_f = 0 \quad (16.8)$$

One can rearrange Eq. (16.8) and find that the effective pressure drop ΔP , balancing the viscous dissipation $\eta\nabla^2 v_f$, along the channels in membrane is given by:

$$\Delta P = \Delta p + \int_{-L/2}^{L/2} c(x)\frac{\partial U(x)}{\partial x} dx \quad (16.9)$$

where is the pressure difference applied externally (say using a pump), by comparing with Eq. (16.5), it follows:

$$\int_{-L/2}^{L/2} c(x)\frac{\partial U(x)}{\partial x} dx = -\Delta\Pi_{\text{eff}} = -\sigma k_B T \Delta c \quad (16.10)$$

This is the Starling equation in the physiology literature. Combining Eqs. (16.7) and (16.10), the rejection factor σ is given by:

$$\sigma = 1 - \frac{L}{\int_{-L/2}^{L/2} \exp\left(\frac{U(x)}{k_B T}\right) dx} \quad (16.11)$$

There are three cases which are of our interests as follows. (i) When $U \gg k_B T$, or there is a very high energy barrier within the membrane for the solute to overcome $\sigma \rightarrow 1$, which means the film is not permeable for solute but permeable for water, giving an osmotic pressure difference following the van't Hoff equation (Eq. (16.4)). (ii) When $U \approx +k_B T$, the membrane remains to be repulsive to solute, giving $0 < \sigma < 1$, so the solvent flow is still in the direction of increasing concentration. (iii) When $U < 0$, or the membrane itself is attractive to solute, yielding $\sigma < 0$. The membrane-induced “negative osmotic pressure” implies that the solvent flow direction would be from high concentration to low concentration. One can imagine that since the membrane accelerate the solute diffusion, there must be a solvent flow induced along the diffusion direction.

Next, under the assumption that the flow across the membrane follows the Darcy's law, namely $\langle v \rangle = -\frac{\kappa \Delta P}{\mu L}$, combining with Eq. (16.9), the relation of the solvent permeance in Eq. (16.5) is obtained, $\mathcal{L}_{\text{hyd}} = \kappa/\eta L$. Here the permeance takes into account of the membrane properties such as pore size and geometry.

Finally, within the membrane, if we neglect the convective term, the solute transport is driven by the spatial gradient of chemical potential $\mu(x)$ (due to the concentration difference) and the membrane potential $U(x)$. Accordingly, one can write the solute flux as follows:

$$N = -uc \frac{\partial}{\partial x}(\mu + U) \quad (16.12)$$

where u is the solute mobility, and $\mu = k_B T \ln(c/c')$ is the chemical potential of the solution, with c' as the reference concentration. Since N is a constant independent of x , the integration of Eq. (16.12) w.r.t. x from $-L/2$ to $L/2$ yields:

$$NL = -u \left(\int_{-L/2}^{L/2} c \frac{\partial \mu}{\partial x} dx - \int_{-L/2}^{L/2} c \frac{\partial U}{\partial x} dx \right) \quad (16.13)$$

The first integral on the right hand side (RHS) yield $k_B T \Delta c$; using Eq. (16.11), the second integral on the RHS is given by $\sigma k_B T \Delta c$. Following the Einstein relation $u = D/(k_B T)$, we have:

$$N = -\frac{D}{L}(1 - \sigma)\Delta c \quad (16.14)$$

Comparing with the second equation of Eq. (16.5), by neglecting the convective contribution, the parameter of solute permeativity $\omega = (1 - \sigma)$. Putting that back to Eq. (16.5), with the membrane characteristic parameters κ and σ , one can describe solute and solvent transport across a membrane, when the concentration and pressure differences are known!

16.2 Inclusion of electric field into the transport matrix

The picture we defined in the previous section only considered the pressure and concentration driven systems. Now we can also include electrical forces and generalize the transport equations into a matrix form (still assuming a linear transport regime, with low solute concentration). Here, we define a transport matrix \mathbb{L} and write the generalized equation by

using the excess solute flux $N - c\langle v \rangle$ instead of N , and preferring the chemical potential of the solute $\mu = k_B T \ln(c)$ instead of the concentration. For electrical effects, we add electric current I and applied electric field $-\nabla\psi$,

$$\begin{pmatrix} \langle v \rangle \\ N - c\langle v \rangle \\ I \end{pmatrix} = \mathbb{L} \times \begin{pmatrix} -\nabla p \\ -\nabla\mu \\ -\nabla\psi \end{pmatrix} \quad (16.15)$$

The matrix \mathbb{L} is symmetric and positive definite due to Onsager principle [5]. The diagonal terms of this matrix relates solvent flux to pressure gradient, solute flux to concentration gradient, and ionic current to applied electric field. The off-diagonal terms indicate the cross effects as indicated in Figure 16.3. The off-diagonal terms of matrix \mathbb{L} can be defined

$$\begin{pmatrix} \langle v \rangle \\ N - c\langle v \rangle \\ I \end{pmatrix} = \begin{pmatrix} \text{Permeability} & \text{Diffusio-osmotic flow} & \text{Electro-osmotic flow} \\ \text{Excess flux under pressure} & \text{Diffusion} & \text{Excess flux under electric field} \\ \text{Streaming ion current} & \text{Diffusio-osmotic ion current} & \text{Electric conductance} \end{pmatrix} \times \begin{pmatrix} -\nabla p \\ -\nabla\mu \\ -\nabla\psi \end{pmatrix}$$

Figure 16.3: Transport matrix as described in Equation (16.15) and its physical origins, with colors indicating the symmetric terms. Adapted from [6]

by the corresponding mobility values, which are dependent on the flow geometry. We can write these terms for the first column: for the electric current and the excess solute flux generated due to a pressure drop as,

$$\begin{aligned} I &= u_{EO} \times (-\nabla p) \\ N - c\langle v \rangle &= u_{DO} \times (-\nabla p) \end{aligned} \quad (16.16)$$

where u_{EO} is the electro-osmotic mobility (for a channel, we have found this value in Lecture 14.3) and u_{DO} is the diffusio-osmotic mobility (for a membrane, we have found it above, in terms of permeance and rejection factor, $u_{DO} = \mathcal{L}_{hyd} \sigma k_B T$). The last off-diagonal term can be written for an electric current generated by a concentration (osmotic) gradient, which can be found for example for a nanochannel separating two reservoirs as [7],

$$I = K_{osm} \times (-\Delta \ln(c_s)) \quad (16.17)$$

where c_s is the salinity ratio of two reservoirs and K_{osm} is the osmotic electric mobility, which depends on the geometry and surface charge profile of the interfacial system and can be found by applying the Poisson-Boltzmann equations to determine electric double layer properties.

16.3 Osmotic diodes and osmotic pressure rectification by external bias

Consider a membrane with nanoscale pores/channels with asymmetric geometry or surface charge profile. Assuming the nanochannel's surface charges play a comparable role to the bulk charges inside, the nanochannel behaves as an ionic diode, rectifying the ionic current versus the applied bias (Figure 16.4). Moreover, such a nanochannel would also have an asymmetric interaction with the solute inside, which in turn means an asymmetric force on the solvent molecules, thereby rectifying the osmotic pressure versus the concentration gradient. In order to quantify the rectification, we can start by the mechanical

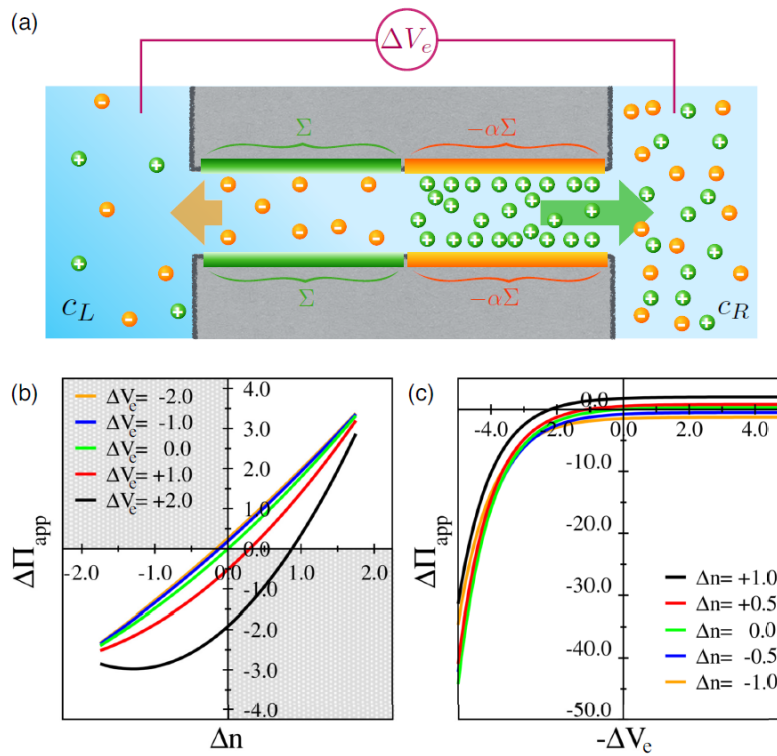


Figure 16.4: Osmotic diode rectification. (a) Schematic of the nanochannel with asymmetric surface charge (Σ) distribution, where $\alpha \neq 1$. Rectification behavior is shown in the plots, for apparent osmotic pressure vs. the salinity gradient (b) and the applied voltage (c). Δn is the normalized concentration difference between the left and right reservoirs. Adapted from [6, 8]

forces driving the solvent, which means writing the Stokes equation,

$$-\nabla p - \rho \nabla V_e + \eta \nabla^2 v_f = 0 \quad (16.18)$$

where A is the cross-section area and L is the length of the nanochannel, ρ is the net charge density (we assume monovalent ions) and V_e is the electric potential. Following a similar

route we employed in section 16.1, by integrating the Stokes equation we can write the solvent flux in terms of the effective pressure,

$$\langle v \rangle = -\frac{A\mathcal{L}_{\text{hyd}}}{L}(p - \Pi_{\text{app}}) \quad (16.19)$$

Combining the last two equations, the apparent osmotic pressure becomes,

$$\Pi_{\text{app}} = -\frac{1}{A} \iint dx dA \rho \nabla V_e \quad (16.20)$$

Now, we can combine the solvent mechanics (Stokes equation) with the solute transport (Poisson Nernst Planck (PNP) equations) and define the solute flux as (again assuming a low Peclet number, as the advection is likely to be negligible due to narrow channel profile),

$$N = -\mathcal{D} \left(\nabla(n_+ + n_-) + \frac{1}{k_B T} (n_+ - n_-) e \nabla V_e \right) \quad (16.21)$$

where n_{\pm} is the normalized ion concentration with the corresponding charge sign. Combining the last two equations, we can write the apparent osmotic pressure in terms of the solute flux as,

$$\Delta \Pi_{\text{app}} = k_B T \left(\Delta n_{\text{sol}} + \frac{L}{D} N \right) \quad (16.22)$$

where $n_{\text{sol}} = n_+ + n_-$ and N is the solute flux along the nanochannel. The full PNP system can be solved analytically (see the supplementary material from [7]) in the regime of high surface charge and the apparent osmotic pressure can be written explicitly as,

$$\Delta \Pi_{\text{app}} = k_B T \left(2 \left(1 - \frac{1}{\delta} \right) \Delta n - \frac{\alpha - 1}{\alpha \delta} \frac{n_R}{n_0} (n_L \exp \left(\frac{e \Delta V_e}{k_B T} \right) - n_R) \right) \quad (16.23)$$

where α is the surface asymmetry factor as shown in Figure 16.4, n_R and n_L are the normalized concentrations on both sides of the nanochannel, n_0 is the bulk concentration in the channel defined as $(n_R + n_L)/2$ and δ is the dimensionless factor indicating the relative importance of the surface charge ($\delta = |\Sigma/(Hn_0)|$), with H being the height of the nanochannel. Hence, at the absence of external pressure the solvent flux becomes,

$$\langle v \rangle = \frac{A\mathcal{L}_{\text{hyd}}}{L} k_B T \sigma (n_L - n_R) + Q_S \left(\exp \left(\frac{e \Delta V_e}{k_B T} \right) - 1 \right) \quad (16.24)$$

where σ is the rejection coefficient, which is a nonlinear function of the reservoir concentrations and can be found directly from the last two equations and Q_S is the limiting solvent flux expressed as,

$$Q_S = \frac{A\mathcal{L}_{\text{hyd}}}{L} k_B T \frac{1 - \alpha n_R n_L}{\alpha \delta n_0} \quad (16.25)$$

The rectification behavior is plotted in Figure 16.4, showing an enhanced rectification at higher applied bias. Under appropriate conditions, this rectification behavior can generate an induced water/solvent flow against the osmotic gradient, which can be maintained over time by applying oscillating voltage bias, thereby enabling new approaches for advanced water purification applications.

References

- (1) Van't Hoff, J. H. *Zeitschrift für Physikalische Chemie* **1890**, 5U, 174–176.
- (2) Kedem, O.; Katchalsky, A. *The Journal of General Physiology* **1961**, 45, 143–179.
- (3) Marbach, S.; Yoshida, H.; Bocquet, L. *The Journal of Chemical Physics* **2017**, 146, 194701.
- (4) Manning, G. S. *The Journal of Chemical Physics* **1968**, 49, 2668–2675.
- (5) Onsager, L. *Physical Review* **1931**, 37, 405–426.
- (6) Marbach, S.; Bocquet, L. *Chemical Society Reviews* **2019**, 48, 3102–3144.
- (7) Siria, A.; Poncharal, P.; Biance, A.-L.; Fulcrand, R.; Blase, X.; Purcell, S. T.; Bocquet, L. *Nature* **2013**, 494, 455–458.
- (8) Picallo, C. B.; Gravelle, S.; Joly, L.; Charlaix, E.; Bocquet, L. *Physical Review Letters* **2013**, 111, DOI: 10.1103/physrevlett.111.244501.

