Lecture 14

Electrokinetic Phenomena

The electrokinetic phenomena refer to the mass t

In an electrolyte solution, the interplay between the electric field and the fluid flow field belongs to a rich family of electrokinetic phenomena. Depending on the origin of driving forces, the electrokinetic phenomena can be categorized into[1] (Figure 14.1):

1. Electroosmosis: fluid flow field due to electric field
2. Electrophoresis: movement of charged species in a flow under an electric field
3. Streaming current / potential: electric field caused by pressure-driven flow
4. Sedimentation potential: electric field caused by the flow around a charged object dragged by gravity

As can be seen, electrokinetic phenomena are in general *second order* phenomena, such that field / flux of type A is induced by field / flux of type B. For instance, in electroosmosis (Figure 14.1a) electric field causes a mechanical motion of fluid, whereas in streaming current / potential (Figure 14.1c) the applied mechanical force to a electrolyte fluid produces an electric current. The same principle applies to electrophoresis (Figure 14.1b) and sedimentation potential (14.1d).

In this lecture we will discuss the fundamental physics behind the electroosmosis, by combining our knowledge of the fluid dynamics and electrostatics of the electrical double layer.

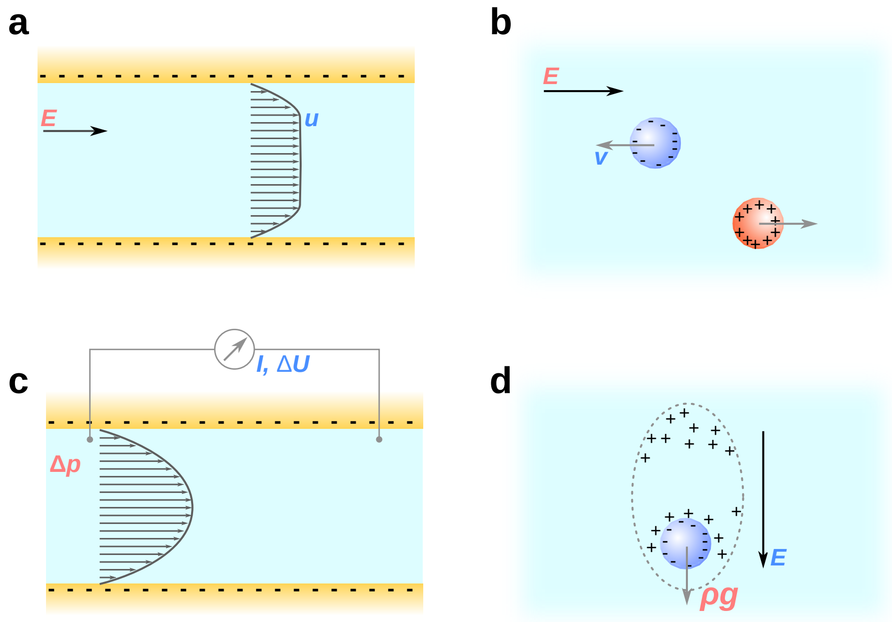

Figure 14.1: Typical electrokinetic phenomena. (a) electroosmosis. (b) electrophoresis. (c) streaming current / potential. (d) sedimentation potential.

14.1 Nernst-Planck equation

The time dependent mass transport equation for a specie i, can be categorized into the flux and reaction terms, such that:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \underbrace{N_i}_{\text{flux}} + \underbrace{R_i}_{\text{reaction}} \tag{14.1}$$

where N_i is the flux and R_i is the reaction rate. Far away from the electrode surface, the reaction term can be ignored. Analogous to the mass transport in fluid, the mass flux equation for ionic specie i in electrokinetic phenomena reads:

$$N_i = \underbrace{c_i v_{\mathrm{f}}}_{\text{fluid flow}} - \underbrace{\mathcal{D}_i \nabla c_i}_{\text{diffusion}} - \underbrace{(u_i z_i e)\nabla \psi c_i}_{\text{electric field}} \tag{14.2}$$

where v_{f} is the velocity field of the fluid, c_i is the molar concentration, $\mathcal{D}_i$ is the diffusivity, u_i is the mobility and z_i is the valency of specie i, respectively. The contribution of each component to the total flux is schematically shown in Figure 14.2.

The flux due to electric field (also known as drift) corresponds with the velocity of specie /i. in the electric field, that:

$$v_i = u_i z_i e E = u_i z_i e \nabla \psi \tag{14.3}$$

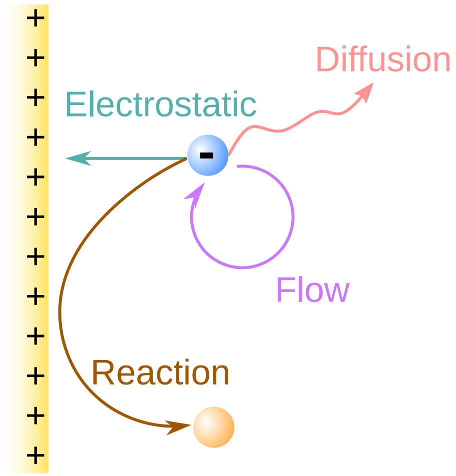

Figure 14.2: Contributions to total flux in electrokinetic phenomena.

In a 1D system at steady state and without fluid flow, the flux for each specie is 0:

$$\begin{aligned}\mathcal{D}_i \frac{\mathrm{d}c_i}{\mathrm{d}x} &= -u_i z_i e \frac{\mathrm{d}\psi}{\mathrm{d}x} c_i \\ \mathcal{D}_i \frac{\mathrm{d}\ln(c_i)}{\mathrm{d}x} &= -u_i z_i e \frac{\mathrm{d}\psi}{\mathrm{d}x}\end{aligned} \tag{14.4}$$

Consider that both $\mathcal{D}_i$ and u_i are constant and $\psi(x = \infty) = 0$, we can express the concentration profile using Boltzmann distribution:

$$c_i(x) = c_{i,0} \exp(-\frac{z_i e \psi u_i}{\mathcal{D}_i}) = c_{i,0} \exp(-\frac{z_i e \psi}{k_\mathrm{B} T}) \tag{14.5}$$

Compare the coefficient in the exponential term, we find the relation between the diffusivity and mobility:

$$u_i = \frac{\mathcal{D}_i}{k_\mathrm{B} T} \tag{14.6}$$

which is known as the Einstein relation.^{2} Plug this into Equation 14.2 we can express the flux use $\mathcal{D}_i$:

$$\begin{aligned}N_i &= c_i v_\mathrm{f} - \frac{\mathcal{D}_i}{k_\mathrm{B} T} c_i [k_\mathrm{B} T \nabla \ln c_i + z_i e \nabla \psi] \\ &= c_i v_\mathrm{f} - \frac{\mathcal{D}_i}{k_\mathrm{B} T} c_i \nabla \mu_i\end{aligned} \tag{14.7}$$

where $\mu_i = k_\mathrm{B} T \ln c_i + z_i e \psi$ is the electrochemical potential of specie i. Equation 14.7 is known as the Nernst-Planck equation. This is the principle equation describing the mass transfer of ionic species in the electrokinetic system. We need further information for both v_i and ψ to solve the Nernst-Planck equation, which will be discussed in the next section.

14.2 Self-consistent Nernst-Planck-Poisson-Stokes equations

The influence of the electric field on the fluid flow is described by adding the electrostatic force into the Navier-Stokes equation:

$$\begin{aligned}\underbrace{\rho(\frac{\partial v_\mathrm{f}}{\partial t} + v_\mathrm{f} \cdot \nabla v_\mathrm{f})}_{\text{0 if steady state and slow flow}} &= \rho g - \nabla p + \mu \nabla^2 v_\mathrm{f} + \frac{F_\mathrm{elec}}{A} \\ &= \underbrace{\rho g}_{\text{gravity}} - \underbrace{\nabla p}_{\text{pressure}} + \underbrace{\mu \nabla^2 v_\mathrm{f}}_{\text{viscous}} + \underbrace{\varepsilon_0 \varepsilon_r \nabla^2 \psi \nabla \psi}_{\text{electrostatic}}\end{aligned} \tag{14.8}$$

The expression for electrostatic force F_elec is taken from Lecture 13 by considering the osmotic pressure of the solution. This term is important when the fluid is near the electrode surface, where both $\nabla \psi$ (electric field) and $\nabla^2 \psi$ (charge density) are non-zero.

The potential of the system is described by the Poisson equation $\nabla^2 \psi = -\rho/\varepsilon_0 \varepsilon_r$. Note due to the existence of external flow, the Boltzmann distribution for ionic species is usually not valid.[3] As a consequence the concentration of ionic species has to be solved by coupling with the mass transport equation. Putting all the pieces (Nernst-Planck (N-P) equation for concentration, Navier-Stokes (N-S) equation for fluid field and Poisson equation for electric potential), we have the self-consistent equation sets describing the mass transfer with electrostatic interactions:

$$\begin{cases} \frac{\partial c_i}{\partial t} = -\nabla \cdot \left[c_i v_\mathrm{f} - \frac{\mathcal{D}_i}{k_\mathrm{B} T} c_i (k_\mathrm{B} T \nabla \ln c_i + z_i e \nabla \psi) \right] & \text{N-P} \\ \rho g - \nabla p + \mu \nabla^2 v_\mathrm{f} + \varepsilon_0 \varepsilon_r \nabla^2 \psi \nabla \psi = 0 & \text{N-S} \\ \nabla^2 \psi = -\frac{\rho}{\varepsilon_0 \varepsilon_r} & \text{Poisson} \\ \nabla \cdot v_\mathrm{f} = 0 & \text{Continuity} \end{cases} \tag{14.9}$$

The equation set is also called as the Nernst-Planck-Poisson-Stokes equations, after the individual named equations. Such equations are numerically solvable but very complicated, due to the highly non-linear term of the electrostatic interaction ($\nabla^2 \psi \nabla \psi$) in the Navier-Stokes equation. A possible simplification is to assume that in a fully developed flow, the charge density ρ is not distorted by the flow. This is not a bad assumption since the boundary layer thickness of the flow is generally much larger than the Debye length λ_D. In other words, we can divide the electrical potential into two parts, namely the "equilibrium" potential ψ_eq created by the equilibrium charge distribution, and the "non-equilibrium" potential ψ_ne caused by the flow, such that $\psi = \psi_\mathrm{eq} + \psi_\mathrm{ne}$. Under such assumption, we have $\rho = \rho_\mathrm{eq} = -\varepsilon_0 \varepsilon_r \nabla^2 \psi_\mathrm{eq}$ and $\nabla^2 \psi_\mathrm{ne} = 0$. We can therefore decouple the velocity field and potential in the Navier-Stokes equation as:

$$\rho g - \nabla p + \mu \nabla^2 v_\mathrm{f} + \varepsilon_r \varepsilon_0 \nabla^2 \psi_\mathrm{eq} \nabla \psi = 0 \tag{14.10}$$

14.3 Electroosmosis in a channel

As an example of the decoupled Navier-Stokes equation, we study the electroosmosis in a parallel-wall channel with width H, as shown in Figure 14.3.

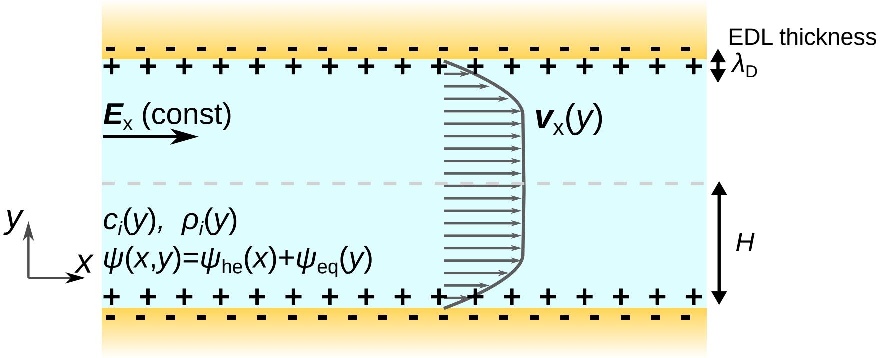

Figure 14.3: Electroosmosis in a channel.

We assume the parallel walls of the channel are negatively charged. The flow passes along the x-direction with $v = (v_x, 0, 0)$ (however v_x also depends on the position y!). At the interface of electrolyte solution, the electric potential is ζ (known as the ζ-potential). The external field created by the charged walls creates ψ_{eq} that is uniform in x-direction, while the flow creates ψ_{ne} that only varies in x-direction:

$$\psi = \psi_{\mathrm{eq}}(y) + \psi_{\mathrm{ne}}(x) \tag{14.11}$$

where both potentials follow:

$$\begin{aligned} \frac{\mathrm{d}^2\psi_{\mathrm{ne}}}{\mathrm{d}x^2} &= 0 \\ \frac{\mathrm{d}^2\psi_{\mathrm{eq}}}{\mathrm{d}y^2} &= -\frac{\rho(y)}{\varepsilon_0\varepsilon_r} \end{aligned} \tag{14.12}$$

Therefore we can solve ψ_{ne} and ψ_{eq} separately:

- ψ_{ne}

  The non-equilibrium potential is linear in x-direction, and has form:

  $$\psi_{\mathrm{ne}} = -E_x x \tag{14.13}$$

- ψ_{eq}

  At equilibrium ρ follows the Boltzmann distribution. If we use the Debye-Hückel approximation, ψ_{eq} has the form:

  $$\psi_{\mathrm{eq}} = \zeta \exp(-\kappa y) \tag{14.14}$$

  Yet more accurate solutions such as the Gouy-Chapman method needs to be used when ζ is large.

Combine the solutions for ψ_{eq} and ψ_{ne}, we can solve the flow velocity in the Navier-Stokes equation. Neglecting the gravity and pressure terms, we have:

$$\begin{aligned}\frac{\partial^2 v_x}{\partial y^2} &= -\frac{\varepsilon_0 \varepsilon_r}{\mu}\frac{\mathrm{d}^2\psi_{\text{eq}}}{\mathrm{d}y^2}\frac{\mathrm{d}\psi_{\text{ne}}}{\mathrm{d}x} \\ &= \frac{\varepsilon_0 \varepsilon_0 E_x \zeta \kappa^2}{\mu}\exp(-\kappa y)\end{aligned} \tag{14.15}$$

The boundary conditions are:

$$\begin{cases} v_x(y=0) = 0 & \text{non-slip} \\ \frac{\partial v_x}{\partial y}(y=H) = 0 & \text{symmetry} \end{cases} \tag{14.16}$$

which gives the final solution for v_x as a function of y:

$$v_x(y) = -\frac{\varepsilon_0 \varepsilon_r E_x \zeta}{\mu}[1 - \exp(-\kappa y)] \tag{14.17}$$

This means, if $H \gg \kappa^{-1}$, the flow has an average flow speed of:

$$v_{\text{infty}} = -\frac{\varepsilon_0 \varepsilon_r \zeta}{\mu}E_x = -u_{\text{eo}}E_{\text{x}} \tag{14.18}$$

where $u_{\text{eo}} = \varepsilon_0 \varepsilon_r \zeta / \mu$ is the effective "flow mobility" of the electrolyte solution, as an analog to the mobility of individual ions. When the characteristic width H of the channel is much larger than the Debye length κ^{-1} (or λ_{D}), the fluid behaves like a plug flow with velocity v_∞ with a slip boundary. As a comparison, the pressure-driven flow has a quadratic profile of velocity along the x-direction, as described by the Poiseulli flow:

$$v_x(y) = -\frac{H^2}{2\eta}(\frac{\partial p}{\partial x})[1 - (\frac{y}{H})^2] \tag{14.19}$$

where η is the dynamic viscosity of the liquid.

One can estimate the magnitude of the electroosmosis flow using Equation 14.18. With ζ= 200 mV, to reach a significant flow at the order of 1 $\text{cm}\cdot\text{s}^{-1}$, one need to apply a voltage drop of ca 70 $\text{V}\cdot\text{m}^{-1}$. As a consequence, in typical electroosmosis setups, the voltage applied across the ends of the channel is usually larger than the electrochemical window and thus gas bubbles are generated. The resistive heating in the channel may also become considerable. Notice in the Equation 14.18, the ζ-potential influences both the magnitude and direction of the flow. Usually in glass-based capillaries, ζ is difficult to be tuned. However, using the technique introduced in Lecture 12, we can use a dielectric layer as the gate on the channel wall and induce ζ by the field effect, which is a technique known as the field effect electroosmosis.[4]

References

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