

Module : 4

External field induced membrane separation processes for colloidal particles:

- fundamentals of various colloid separation
- derivation of profile of electric field strength
- coupling with membrane separation and electrophoresis

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External field induced membrane separation processes for colloidal particles

4.1 Fundamentals of various colloid separation processes

Electrokinetic Effects:

When one charged phase is caused to have a relative velocity past the second phase, a number of phenomenon occur. These phenomena are grouped under “**Electrokinetic effects**”.

Origin of Electrokinetic effect:

If a charge phase (I) is placed next to another phase (II), in phase II, there is an excess charge close to the interface and the balancing charge is distributed.

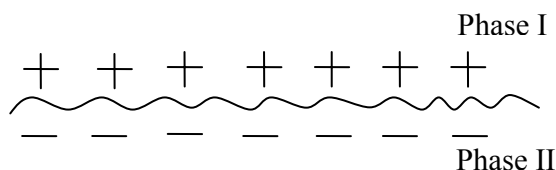


Fig. 4.1: Schematic of co-existence of two phases having different charges

For a positively charged surface in an electrolytic solution, negative charges accumulate close to interface and their concentration reduces away from the surface to the bulk. Electrostatic potential is taken as zero in the bulk. The bulk is situated far from the charged surface, i.e., 5-200 nm from the surface depending on electrolytic concentration. Arrangement/distribution of charges from interface to the bulk is known as Electrical double layer at the interface.

Categories of Electrokinetic effects

There are four distinct effects depending on the way in which motion is induced:

1. Electrophoresis
2. Electro-osmosis
3. Streaming potential
4. Sedimentation potential

Electrophoresis:

If one phase is liquid (or gas) in which the second phase is suspended as particles as solids (or liquid), then the particles can be induced to move by applying an external electric field across the system. This is known as *Electrophoresis*.

Measurement of velocity of particles under a known external field gives information about their net electric charge or their surface potential with respect to bulk of the suspending phase.

Electroosmosis:

When solid remains stationary and the liquid move in response to an applied electric field, the phenomenon is known as *Electroosmosis*. It occurs when solid is in the form of a capillary or porous plug which is filled with liquid. Applied field acts upon the charges (usually ions) in the liquid as they move in response to the field they drag the liquid along with them.

Measurement of velocity of liquid or volume transported per unit current flow, gives information about the net surface charge or the electrical potential in the neighbourhood of the wall.

Streaming potential:

Instead of applying an electric field to cause the liquid to move through a capillary/porous plug, one can force the liquid to move under a pressure gradient. Excess charges near the wall are carried away by the liquid and there is an accumulation in the downstream causing the build up of an electric field which drives an electric current back (by ionic contraction through the liquid) against the flow direction. A steady state is reached and the measured potential difference across the capillary/plug is called Streaming potential. It is related to driving pressure and potential in the neighbourhood of the wall.

Sedimentation potential:

When charged colloidal particles are allowed to settle (or rise) through a fluid under gravity or centrifugal field, a potential difference is generated, known as Sedimentation potential. Measurement of sedimentation potential

Surface of shear and Zeta potential:

In electrophoresis, particles (sphere, cylinder, etc.) move in the liquid. Surface of shear is an imaginary surface which is considered to lie close to the solid charged surface and within which fluid is stationary or having infinite viscosity. This thin layer of fluid is known as Stern layer. So, when particles move, they take an envelope of fluids with counter charges with it. The potential on this outer surface is known as *Zeta potential*. Measurement of electrophoretic mobility (velocity/field strength) gives a measure of net charge on the solid particle.

Significance of Zeta potential:

Many colloidal systems are determined by particle charge (or potential). Potential distribution determines the interaction energy between particles, it is responsible for stability towards coagulation, sedimentation behaviour, flow behaviour of mineral ores, etc.

Concentration profiles of ions in electrolytic solution in presence of a charged surface

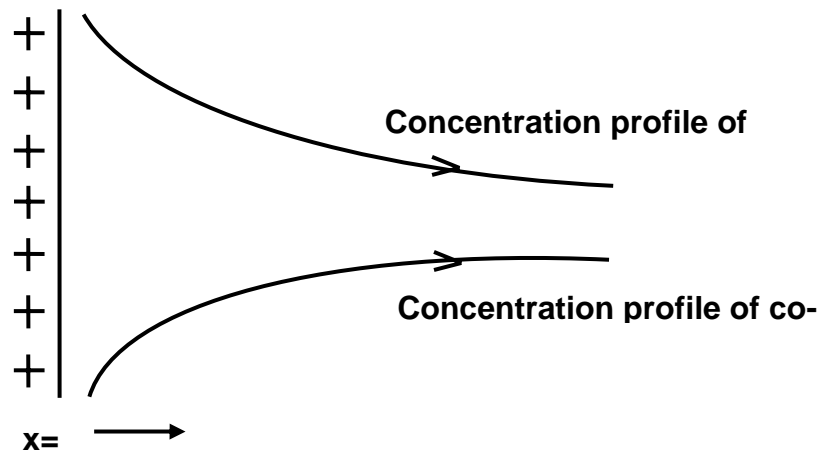


Fig. 4.2: Charge distribution in an electrolytic solution from a charged surface

Consider a positively charged surface immersed in an electrolyte solution. Counter ion concentration will be more towards the surface and decrease towards bulk of the solution. In the bulk ($x \rightarrow \infty$), electro neutrality is maintained such that

$$\text{at } x=\infty, \quad z^+ n_0^+ + z^- n_0^- = 0 \quad (4.1)$$

Where, z^+ is the valency of cations; z^- is the valency of anions; n_0^+ and n_0^- are the number concentration of these ions (number/m³) in the bulk.

$$|z^+| n_0^+ + |z^-| n_0^- = 0 \quad (4.2)$$

Potential energy of an ion in an electric field at a distance x is

$$\phi(x) = ze\psi(x) \quad (4.3)$$

Where, $\psi(x)$ is the potential of ion at x . At the steady state, net ionic flux at any cross section is zero. The ionic flux J contains two components, namely, (i) flux due to concentration gradient and (ii) flux due to electric potential gradient.

$$J = - \left[D \frac{dn}{dx} + \frac{n}{f} \frac{d\phi}{dx} \right] \quad (4.4)$$

Where, f is friction factor that is a function of geometry, size of solute, etc. At steady state,

$$-\frac{dn}{n} = \frac{d\phi}{fD} \quad (4.5)$$

Where, $f = \frac{K_B T}{D}$ from Stokes-Einstein equation.

K_B = Boltzmann constant.

Integrating Eq.(4.5), the following expression is obtained.

$$\int_{n_0}^{n(x)} \frac{dn}{n} = - \frac{1}{K_B T} \int_0^{\phi(x)} d\phi$$

$$n(x) = n_0 \exp \left(- \frac{\phi(x)}{K_B T} \right) \quad (4.6)$$

The above distribution is known as Boltzmann distribution.

Charge density

Concentration profile of i^{th} type ion is given by,

$$n_i = n_{i0} \exp\left(-\frac{z_i e \psi}{K_B T}\right) \quad (4.7)$$

Where, $\psi = \psi(x)$. For counter ions, z_i is negative and for the co-ions it is positive in case of positively charged surface. Thus, the concentration distribution of counter and co ions become,

$$n_i |_{\text{counter ion}} = n_{i0} \exp\left(\frac{z_i e \psi}{K_B T}\right) \quad (4.8)$$

$$n_i |_{\text{co-ion}} = n_{i0} \exp\left(-\frac{z_i e \psi}{K_B T}\right) \quad (4.9)$$

For a symmetric electrolyte, like NaCl, $|z_+| = |z_-| = z$ and for positively charged surface, the concentration profiles of co and counter ions are as follows:

$$n_+ = n_{+0} \exp\left(-\frac{ze\psi}{K_B T}\right) \quad (4.10)$$

$$n_- = n_{-0} \exp\left(+\frac{ze\psi}{K_B T}\right) \quad (4.11)$$

The net charge density in solution (number/volume) becomes

$$\rho = \sum z_i e n_i \quad (4.12)$$

For symmetric electrolyte:

$\rho = |z| e (n^+ - n^-)$ and the expression of charge density becomes

$$\rho = \sum z_i e n_{i0} \exp\left(-\frac{z_i e \psi(x)}{K_B T}\right) \quad (4.13)$$

Potential distribution

Flat plate model:

If the charged surface is a flat plate and has an electrostatic potential ψ_0 , the compensation ions are regarded as point charges. The potential distribution is given by *Poisson's equation*.

$$\rho = \text{div}(-\epsilon \text{grad} \psi) \quad (4.14)$$

Where, ρ is the charge density; ψ is the potential, ϵ is the dielectric constant of the medium.

$$\epsilon = \epsilon_0 D \quad (4.15)$$

ϵ_0 is Permittivity in vacuum and D is the dielectric constant and it is about 80 for water.

For constant value of dielectric constant, the Poisson's equation becomes,

$$\nabla^2 \psi = -\frac{\rho}{\epsilon} \quad (4.16)$$

In planar coordinate, and inserting the expression of charge density from Eq.(4.13), the above equation becomes,

$$\frac{d^2 \psi}{dx^2} = -\frac{\rho}{\epsilon} \sum_i z_i n_{i0} \exp\left(-\frac{z_i e \psi}{K_B T}\right) \quad (4.17)$$

The above equation is called *Poisson-Boltzman equation*. If ψ is small within double layer (i.e. $ze\psi/K_B T \ll 1$), the above equation is simplified to,

$$\frac{d^2 \psi}{dx^2} = -\frac{1}{\epsilon} \left[\sum_i z_i e n_{i0} - \sum_i z_i^2 e^2 \frac{n_{i0} \psi}{K_B T} \right] \quad (4.18)$$

This approximation is known as “*Debye-Huckle approximation*”. This is valid typically for a surface potential, 25 mV.

From the electro neutrality condition the first term in Eq.(4.18) becomes zero and the following equation is resulted.

$$\frac{d^2\psi}{dx^2} = \frac{1}{\epsilon K_B T} \sum z_i^2 e^2 n_{i0} \psi \quad (4.19)$$

By rearranging the above equation, we get the following equation.

$$\frac{d^2\psi}{dx^2} = \kappa^2 \psi \quad (4.20)$$

$$\text{Where, } \kappa = \sqrt{\frac{e^2 \sum z_i^2 n_{i0}}{\epsilon K_B T}} = (\text{Debye length})^{-1}$$

By integrating the above equation with the boundary conditions

$$\text{at } x \rightarrow \infty, \quad \psi = 0 \quad (4.21)$$

$$\text{at } x=0, \quad \psi = \psi_0 \quad (4.22)$$

The potential distribution now becomes,

$$\psi = \psi_0 e^{-\kappa x} \quad (4.23)$$

Where, κ is the compression of double layer and $1/\kappa$ is the double layer thickness. Large value of κ indicates compact of double layer and smaller κ denotes diffused double layer.

More generalized solution for z:z electrolyte in flat plate geometry

The Poisson Boltzman equation for a z:z electrolyte is

$$\frac{d^2\psi}{dx^2} = -\frac{1}{\epsilon} \sum_i z_i n_{i0} \exp\left(-\frac{z_i e \psi}{K_B T}\right) \quad (4.24)$$

Multiply both sides by $2d\psi/dx$ and integrating the following equation is resulted

$$\int_{-\infty}^x 2 \frac{d\psi}{dx} \frac{d\psi}{dx} dx = -\frac{1}{\epsilon} \int_{\psi=0}^{\psi} \sum_i z_i n_{i0} \exp\left(-\frac{z_i e\psi}{K_B T}\right) d\psi \quad (4.25)$$

$$\begin{aligned} \left(\frac{d\psi}{dx}\right)^2 &= -\frac{2}{\epsilon} \sum_i n_{i0} z_i \int_0^{\psi} \exp\left(-\frac{z_i e\psi}{K_B T}\right) d\psi \\ &= \frac{2K_B T}{\epsilon} \sum_i n_{i0} \left[\exp\left(-\frac{z_i e\psi}{K_B T}\right) - 1 \right] \end{aligned} \quad (4.26)$$

For symmetric electrolyte, $z_+ = -z_-$ and $|z_+| = |-z_-| = z$, the above equation is,

$$\left(\frac{d\psi}{dx}\right)^2 = \frac{2K_B T n_0}{\epsilon} \left[\exp\left(\frac{ze\psi}{K_B T}\right) + \exp\left(-\frac{ze\psi}{K_B T}\right) - 2 \right] \quad (4.27)$$

The above equation can be simplified as,

$$\frac{d\psi}{dx} = -\frac{2\kappa K_B T}{ze} \sinh\left(\frac{ze\psi}{2K_B T}\right) \quad (4.28)$$

After integration, the following equation is resulted.

$$\tanh\left(\frac{\overline{z\psi}}{4}\right) = \tanh\left(\frac{\overline{z\psi_0}}{4}\right) \exp(-\kappa x) \quad (4.29)$$

Where, $\overline{\psi} = \frac{e\psi}{K_B T}$

For $\psi_0 < 30$ mv, by expanding exponential term the expression is reduced to

$$\psi = \psi_0 \exp(-\kappa x) \quad (4.30)$$

Double layer around charged sphere

In various engineering applications, we consider the motion of a charged sphere in an electrolytic solution, for example, filtration of a protein solution. Every protein is charged and we can manipulate their charge by setting the operating pH. If the operating pH is set above the characteristic isoelectric point (pH at which protein is charge less), protein is

negatively charged and if it is set below the isoelectric point, it is positively charged.

Thus, under Debye-Huckel approximation, the potential distribution in spherical coordinate is presented as,

$$\frac{1}{r^2} \frac{d\left(r^2 \frac{d\psi}{dr}\right)}{dr} = \kappa^2 \psi \quad (4.31)$$

Using the substitution, $\psi = u/r$, the solution of the above equation becomes,

$$\psi = \frac{A}{r} e^{\kappa r} + \frac{B}{r} e^{-\kappa r} \quad (4.32)$$

Using the boundary conditions, $\psi \rightarrow 0$, as $r \rightarrow \infty$ and $\psi = \psi_0$ at $r=a$, the final solution of potential becomes,

$$\psi = \psi_0 \left(\frac{a}{r} \right) \exp[-\kappa(r-a)] \quad (4.33)$$

Estimation of charge on sphere

Charge on the particles must be balanced by that in double layer and can be estimated by a charge balance,

$$Q = - \int_{r=a}^{\infty} 4\pi r^2 \rho \, dr \quad (4.34)$$

Substituting the expression of charge density from Eq.(4.13), the above equation becomes,

$$Q = - \int_{r=a}^{\infty} 4\pi r^2 \, dr \sum n_{i0} z_i e \exp\left(-\frac{z_i e \psi}{K_B T}\right) \quad (4.35)$$

Using Debye-Huckel approximation, the above equation simplifies to,

$$Q = - \int_{r=a}^{\infty} 4\pi r^2 \, dr \sum n_{i0} z_i e \left(1 - \frac{z_i e \psi}{K_B T} \right)$$

$$\begin{aligned}
 &= \int_{r=a}^{\infty} 4\pi r^2 dr \sum \frac{z_i e^2 n_{i0}}{\epsilon K_B T} \psi \\
 &= 4\pi \kappa^2 \epsilon \int_a^{\infty} r^2 \psi dr \\
 &= 4\pi \kappa^2 \epsilon \int_a^{\infty} \psi_0 a \exp(-\kappa[r-a]) r dr \\
 &= 4\pi \epsilon a (1 + \kappa a) \psi_0
 \end{aligned} \tag{4.36}$$

Thus, the surface potential of the charged sphere can be expressed by its surface charge as,

$$\psi_0 = \frac{Q}{4\pi \epsilon a (1 + \kappa a)} \tag{4.37}$$

If we consider ‘ a ’ as radius out to the shear plane, $\psi_0 = \psi$ the surface potential becomes zeta potential as that is the potential exposed to the electrolytic solution. Hence, the zeta potential can be estimated by replacing Q in Eq.(4.37) by effective charge on the outermost surface of the sphere (Q_e),

$$\xi = \frac{Q_e}{4\pi \epsilon a (1 + \kappa a)} \tag{4.38}$$

Electrophoresis:

Case 1: For $\kappa a \ll 1.0$

The electrostatic force applied on the charged particle in presence of external electric field strength E , is given by,

$$F_e = qE \tag{4.39}$$

The viscous force under Stokes regime, felt by the particle is presented as,

$$F_{vis} = 6\pi\mu Rv \tag{4.40}$$

Hence, the electrophoretic velocity is estimated as,

$$v = \frac{qE}{6\pi\mu R} \quad (4.41)$$

The electrophoretic mobility is defined as

$$u = \frac{v}{E} = \frac{q}{6\pi\mu R} \quad (4.42)$$

Replacing Q from Eq.(4.38), the expression of mobility is obtained as,

$$u = \frac{2}{3} \frac{\epsilon \xi}{\mu} \quad (4.43)$$

Case 2: For $\kappa R \gg 1.0$

This is a case of compact double layer. Hence, the curvature of the sphere can really be neglected and we consider the electrolytic solution including the charged sphere as a continuum (as shown in Fig. 4.3) and one can fix the coordinate system on a flat plane.

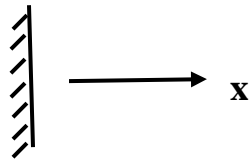


Fig. 4.3: Coordinate system

Thus, the x -component equation of motion becomes under Stokes flow regime (neglecting the inertial terms in Navier-Stokes equation and pressure gradient),

$$\mu \frac{d^2 v}{dx^2} = \rho E \quad (\text{No Pressure gradient/inertial term} \rightarrow \text{small}) \quad (4.44)$$

Invoking the Poisson's equation (Eq. **), and replacing the charge density in Eq. (44), one get the following equation of velocity,

$$\mu \frac{d^2 v}{dx^2} = -\epsilon E \frac{d^2 \psi}{dx^2} \quad (4.45)$$

Integration of the above equation leads to the following expression of electrophoretic mobility,

$$\mu v = \epsilon E \xi$$

$$u = \frac{v}{E} = \frac{\epsilon \xi}{\mu} \quad (4.46)$$

The above equation is known as Helmholtz-Smolouchoski equation.

Coupling with ultrafiltration system

Using the concept of the electrophoretic mobility of charged spheres in electrolytic solution under an external electric field, one can enhance the performance of the ultrafiltration system. This is quite important in case of filtration involving charged macrosolutes, like proteins, micelles, colloids like silica, etc. During ultrafiltration, these charged solutes deposit over the membrane surface, forming a gel type of layer (in case of gel controlling filtration) or a concentrated layer of solutes (in case of osmotic pressure controlled filtration). With the application of an external electric field with suitable polarity, the deposited charged particles migrate from the membrane surface and thus reducing the concentration polarization and enhancing the throughput of the process. Following are the formulation of electric field enhanced ultrafiltration systems.

Gel layer controlling ultrafiltration

Such cases may be observed in filtration of charged macromolecules like pectin, surfactant micelles, etc. The governing equation of such system is given as,

$$(v_w - v_e)c + \frac{dc}{dy} = 0 \quad (4.47)$$

The above equation can be solved with the boundary conditions that at $y=0$, $c=c_g$ and $y=\delta$, $c=c_0$. The solution of Eq. (4.47) becomes,

$$v_w = k \ln \left(\frac{c_g}{c_0} \right) + v_e \quad (4.48)$$

Where, v_e is the electrophoretic mobility and should be calculated from either Eq.(4.41) or Eq.(4.46), depending on the zeta potential on the macroion. Eq.(4.48) clearly shows an enhancement in permeate flux with external electric field strength as electrophoretic mobility is proportional to electric field strength.

Osmotic pressure controlling ultrafiltration

Such cases are important in case of filtration of protein solution or polyelectrolytic solution. In such cases, the governing equation is modified as,

$$u \frac{\partial c}{\partial x} - (v_w - v_e) \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial^2 y} \quad (4.49)$$

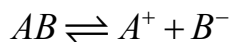
The boundary conditions of Eqs.(4.49) remain same as shown in earlier chapter but the boundary condition at the membrane surface has to be modified as

$$\text{At } y=0, (v_w - v_e)c + D \frac{\partial c}{\partial y} = 0 \quad (4.50)$$

These set of equations have to be solved with the osmotic pressure relationship (Eq.3.36) to predict the filtration performance.

Solved Problems

1. Find out Debye length for 0.01 (M) NaCl solution



$$\kappa^2 = \frac{e^2 \sum z_i^2 n_{i0}}{\epsilon K_B T}$$

n_{i0} = no. of ions/ m³ solution

$$= 1000 M_i N_A$$

Where, M_i = Molar concentration = 0.01 M; N_A = Avagadro's number = 6.023×10^{23} ;

$e = 1.6 \times 10^{-19}$ Coulomb; $\epsilon = \epsilon_0 D$; D = dielectric constant = 80 (for water); K_B = Boltzman

constant = 1.38×10^{-23} J/K; T = temperature = 300 °K; ϵ_0 = permittivity in vacuum = 8.85×10^{-12}

C V⁻¹ m⁻¹.

$$\kappa^2 = e^2 1000 N_A \sum \frac{M_i z_i^2}{\epsilon K_B T}$$

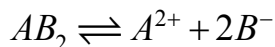
$$= 1000 N_A e^2 \frac{M + M}{\epsilon K_B T}$$

$$= 2000 N_A M e^2 / \epsilon K_B T$$

$$= 1.05 \times 10^{15}$$

$$\kappa^{-1} = 30.8 \text{ \AA}$$

For a 2:1 electrolyte



$$\sum z_i^2 M_i = 4M + M + M = 6M$$

Here anion dissociated into 2 ions. For this

$$\kappa^{-1} = 17.6 \text{ \AA}$$

For 3:1 electrolyte

$$\kappa^{-1} = 12.4 \text{ \AA}$$

2. A protein solution in 0.15(M) NaCl is ultrafiltered with mass transfer coefficient 2×10^{-5} m/s. Filtration is gel layer controlled. Feed concentration is 10 kg/m^3 and gel concentration is 300 kg/m^3 . The charge number on protein is 10e and it has a radius 5 nm.

(a) What will be the permeate flux?

(b) If an external electric field of 400 v/m is applied, what is the permeate flux?

$$\kappa^2 = \frac{2000 N_A M e^2}{\epsilon K_B T}$$

$$M = 0.15 \text{ (M)}$$

$$\kappa^2 = \frac{2000 \times 6.023 \times 10^{23} \times 0.15 \times (1.6 \times 10^{-19})^2}{80 \times 8.85 \times 10^{-12} \times 1.38 \times 10^{-23} \times 300}$$

$$\kappa^{-1} = 7.96 \times 10^{-10} \text{ m}$$

v_E = electrophoretic velocity

$$= \frac{\epsilon \xi}{\mu} E$$

$$\xi = \frac{Q_e}{4\pi\epsilon a(1 + \kappa a)}$$

$$Q_e = 10 \times 1.6 \times 10^{-19} \text{ C} = 1.6 \times 10^{-18} \text{ C}$$

$$\kappa a = (7.96 \times 10^{-10})^{-1} \times 5 \times 10^{-9} = 6.28$$

$$\xi = \frac{1.6 \times 10^{-18}}{4 \times \pi \times 80 \times 8.85 \times 10^{-12} \times 5 \times 10^{-9} \times 7.28}$$

$$= 4.94 \text{ mV}$$

$$v_E = \frac{80 \times 8.85 \times 10^{-12} \times 4.94 \times 10^{-3}}{10^{-3}} \times 400$$

$$= 1.4 \times 10^{-6} \text{ m/s}$$

$$(a) \quad \text{Permeate flux} = K \ln \frac{C_g}{C_0} = 2 \times 10^{-5} \times \ln \frac{300}{10} = 6.8 \times 10^{-5} \frac{m^3}{m^2.s}$$

$$(b) \quad \text{Permeate flux in presence of electric field} = 6.8 \times 10^{-5} + 1.4 \times 10^{-6} \\ = 6.94 \times 10^{-5} \frac{m^3}{m^2.s}$$

3. A protein solution in 0.05(M) NaCl is ultrafiltered with mass transfer coefficient 5×10^{-5} m/s. Filtration is gel layer controlled. Feed concentration is 10 kg/m^3 and gel concentration is 400 kg/m^3 . The charge number on protein is $10e$ and it has a radius 5 nm .

(a) What will be the permeate flux?

(b) If an external electric field of 300 v/m is applied, what is the permeate flux?

$$\kappa^2 = \frac{2000 N_A M e^2}{\epsilon K_B T}$$

$$N_A = 6.023 \times 10^{23}; \quad M = 0.05(M); \quad e = 1.6 \times 10^{-19}$$

$$\epsilon = 80 \times 8.85 \times 10^{-12}; \quad K_B = 1.38 \times 10^{-23}; \quad T = 300 \text{ K}$$

$$\kappa^2 = \frac{2000 \times 6.023 \times 10^{23} \times 0.05 \times (1.6 \times 10^{-19})^2}{80 \times 8.85 \times 10^{-12} \times 1.38 \times 10^{-23} \times 300}$$

$$\kappa = 7.25 \times 10^8 \text{ m}^{-1}$$

$$(a) \quad \text{Permeate flux} = K \ln \frac{C_g}{C_0}$$

$$= 5 \times 10^{-5} \times \ln \frac{400}{10}$$

$$= 18.44 \times 10^{-5} \frac{m^3}{m^2.s}$$

$$(b) \quad E = 300 \text{ V/m}$$

$$\begin{aligned}\xi &= \frac{Q_e}{4\pi\epsilon a(1+\kappa a)} \\ &= \frac{1.6 \times 10^{-19}}{4 \times \pi \times 80 \times 8.85 \times 10^{-12} \times 5 \times 10^{-9} \times (1 + 7.25 \times 10^8 \times 5 \times 10^{-9})} \\ &= 7.78 \text{ mV} \\ v_E &= \frac{\epsilon \xi}{\mu} E = \frac{80 \times 8.85 \times 10^{-12} \times 7.78 \times 10^{-3}}{10^{-3}} \times 300 \\ &= 1.65 \times 10^{-6} \text{ m/s}\end{aligned}$$

$$\text{Permeate Flux} = 18.44 \times 10^{-5} + 1.65 \times 10^{-6}$$

$$= 1.86 \times 10^{-4} \frac{m^3}{m^2.s}$$

4. A positively charged spherical particle of mass m is placed at the bottom of a tall vertical tank filled up completely by 10^{-4} (M) NaCl solution. Particle radius is 100 \AA and density ρ_p , 2000 kg/m^3 . Take solution density (ρ_w) as 1000 kg/m^3 . The zeta potential of the particle is measured and is found out to be $\xi \text{ mV}$. A suitable electric field is applied between the top and the bottom of the vessel so that the particle is attracted and moves up.
- Find the minimum field strength (in V/m) so that the particle is lifted up.
 - Now, a field strength, of the magnitude twice the minimum values ($E=2E_{\min}$) is applied. Obtain an expression of the velocity variation of the particle with time.
 - In (ii), will the particle attain a terminal velocity? If so, what is v_t (terminal velocity)?

Solution:

- Let minimum field strength E_{\min}

$$Q_e = \xi \times 4\pi\epsilon a(1 + \kappa a)$$

At minimum field strength,

$$\sum F_y = 0$$

$$F_B + F_e - mg = 0$$

$$F_e = mg - F_B$$

$$F_B = \text{Buoyant force} = \left(\frac{m}{\rho_p} \right) \rho_w g$$

$$F_e = mg - \frac{m}{\rho_p} \rho_w g$$

$$Q_e E_{\min} = mg \left(1 - \frac{\rho_w}{\rho_p} \right)$$

$$E_{\min} = \frac{mg}{Q_e} \left(1 - \frac{\rho_w}{\rho_p} \right) = \frac{mg}{\xi \times 4\pi\epsilon a(1 + \kappa a)} \left(1 - \frac{\rho_w}{\rho_p} \right)$$

(ii) $E = 2E_{\min}$

$$m \frac{dv}{dt} = F_B + F_e - mg - \text{friction}$$

$$F_B = \frac{m\rho_w}{\rho_p} g$$

$$F_e = Q_e E$$

$$\text{friction} = 6\pi\mu a v$$

$$m \frac{dv}{dt} = \frac{m\rho_w}{\rho_p} g - mg + Q_e E - 6\pi\mu a v$$

$$\frac{dv}{dt} = \left(\frac{\rho_w}{\rho_p} - 1 \right) g + Q_e E - 6\pi\mu a v$$

$$\frac{dv}{dt} = Q_e E - \left(1 - \frac{\rho_w}{\rho_p}\right) g - 6\pi\mu a v$$

$$\frac{dv}{Q_e E - \left(1 - \frac{\rho_w}{\rho_p}\right) g - 6\pi\mu a v} = dt$$

$$\text{Let, } Q_e E - \left(1 - \frac{\rho_w}{\rho_p}\right) g - 6\pi\mu a v = z$$

$$dv = -\frac{dz}{6\pi\mu a}$$

$$\Rightarrow -\frac{dz}{6\pi\mu a z} = dt$$

$$\frac{dz}{z} = -6\pi\mu a \, dt$$

$$z = c_1 \exp(-6\pi\mu a t)$$

$$Q_e E - \left(1 - \frac{\rho_w}{\rho_p}\right) g - 6\pi\mu a v = c_1 \exp(-6\pi\mu a t)$$

$$\text{At } t=0, \quad v=0 \quad \Rightarrow \quad c_1 = Q_e E - \left(1 - \frac{\rho_w}{\rho_p}\right) g$$

$$Q_e E - \left(1 - \frac{\rho_w}{\rho_p}\right) g - 6\pi\mu a v = \left[Q_e E - \left(1 - \frac{\rho_w}{\rho_p}\right) g \right] \exp(-6\pi\mu a t)$$

$$6\pi\mu a v = \left[Q_e E - \left(1 - \frac{\rho_w}{\rho_p}\right) g \right] [1 - \exp(-6\pi\mu a t)]$$

$$v(t) = \frac{Q_e E - \left(1 - \frac{\rho_w}{\rho_p}\right) g}{6\pi\mu a} [1 - \exp(-6\pi\mu a t)]$$

(iii) For terminal velocity;

$$v = v_t \text{ and } \frac{dv}{dt} = 0$$

$$6\pi\mu a v_t = \left(\frac{\rho_w}{\rho_p} - 1 \right) g + Q_e E$$

$$v_t = \frac{1}{6\pi\mu a} \left[Q_e E - \left(1 - \frac{\rho_w}{\rho_p} \right) g \right]$$

5. Solution of protein A with 0.15 (M) NaCl and 30°C is ultrafiltered in a rectangular channel of equivalent diameter 2mm, length 50 cm, cross flow velocity 0.3 m/s and diffusivity $6 \times 10^{-11} \text{ m}^2/\text{s}$. Filtration is gel layer controlled. Feed concentration is 10 kg/m^3 and gel concentration is 300 kg/m^3 . Protein A has surface charge $Q=20e$ (e is the electronic charge in coulomb) and radius is 2nm.

- (i) What will be the permeate flux?
- (ii) Now a suitable external electric field of strength 400 volt/m is applied to increase the permeate flux. What will be the steady state flux now? Assume protein molecules as spherical particles and mobility of the particles is independent of the protein concentration.
- (iii) A protein B of surface charge 30e, radius 50Å and diffusivity $8 \times 10^{-11} \text{ m}^2/\text{s}$ is filtered in the same filtration cell. It also forms a gel with gel concentration 250 kg/m^3 at the same feed concentration. What strength of the electrolyte NaCl needs to be added in order to get the same flux value of A as in part (ii) under the same external field strength?

Data: $N_{av}=6.023 \times 10^{23}$; $\epsilon=80 \times 8.85 \times 10^{-12}$ SI unit; k (Boltzman const) = 1.38×10^{-23} J/K.

Solution viscosity is 10^{-3} Pa-s.

Solution:

0.15 (M) NaCl solution,

$$\text{So, } \kappa^{-1} = 7.96 \times 10^{-10} \text{ m}$$

$$\xi = \frac{Q_e}{4\pi\epsilon a(1+\kappa a)}$$

$$a = 20 \text{ nm} = 2 \times 10^{-9} \text{ m}$$

$$Q_e = 20e$$

$$= \frac{20 \times 1.6 \times 10^{-19}}{4 \times \pi \times 80 \times 8.85 \times 10^{-12} \times 2 \times 10^{-9} \times \left(1 + \frac{2 \times 10^{-9}}{7.96 \times 10^{-10}}\right)}$$

$$= 0.051 \text{ Volt}$$

v_E = electrophoretic velocity

$$= \frac{\epsilon \xi}{\mu} E$$

For $E=400 \text{ V/m}$;

$$v_E = \frac{80 \times 8.85 \times 10^{-12} \times 0.051}{10^{-3}} \times 400$$

$$= 1.44 \times 10^{-5} \text{ m/s}$$

$$(i) \quad d_e = 2 \times 10^{-3} \text{ m}; \quad L = 0.5 \text{ m}; \quad u_0 = 0.3 \text{ m/s}; \quad D = 6 \times 10^{-11} \text{ m}^2/\text{s}$$

$$Sh = \frac{Kd_e}{D} = 1.85 \left(\text{Re} Sc \frac{d_e}{L} \right)^{1/3}$$

$$\frac{kd_e}{D} = 1.85 \left(\frac{u_0 d_e}{\nu} \cdot \frac{\nu}{D} \cdot \frac{d_e}{L} \right)^{1/3}$$

$$k = 1.85 \left(\frac{u_0 D^2}{d_e L} \right)^{1/3}$$

$$= 1.85 \left(\frac{0.3 \times 36 \times 10^{-22}}{2 \times 10^{-3} \times 0.5} \right)^{1/3}$$

$$k = 1.9 \times 10^{-6} \text{ m / s}$$

$$\text{Permeate flux} = k \ln \frac{C_g}{C_0}$$

$$= 1.9 \times 10^{-6} \ln \frac{300}{10}$$

$$= 6.46 \times 10^{-6} \frac{m^3}{m^2.s}$$

(ii) Total flux in presence of 400 V/m

$$= 1.44 \times 10^{-5} + 6.46 \times 10^{-6}$$

$$= 2.09 \times 10^{-5} \frac{m^3}{m^2.s}$$

(iii) Protein B:

$$Q_e = 30 \times 1.6 \times 10^{-19} C; \quad a = 50 \text{ \AA} = 50 \times 10^{-10} \text{ m}; \quad D = 8 \times 10^{-11} \text{ m}^2 / s$$

$$k = 1.85 \left(\frac{0.3 \times 64 \times 10^{-22}}{2 \times 10^{-3} \times 0.5} \right)^{1/3} = 2.3 \times 10^{-6} \text{ m / s}$$

$$2.09 \times 10^{-5} = 2.3 \times 10^{-6} \ln \left(\frac{250}{10} \right) + \frac{\varepsilon \xi}{\mu} E$$

$$2.09 \times 10^{-5} = 7.4 \times 10^{-6} + \frac{80 \times 8.85 \times 10^{-12} \xi}{10^{-3}} E$$

$$1.35 \times 10^{-5} = 7.08 \times 10^{-7} \xi E$$

$$E = \frac{1.35 \times 10^{-5}}{7.08 \times 10^{-7} \xi}$$

$$\xi = \frac{Q_e}{4\pi\epsilon a(1 + \kappa a)}$$

$$= \frac{30 \times 1.6 \times 10^{-19}}{4 \times \pi \times 80 \times 8.85 \times 10^{-12} \times 50 \times 10^{-10} \times \left(1 + \frac{5 \times 10^{-9}}{7.96 \times 10^{-10}}\right)}$$

$$= \frac{0.11}{1 + 6.28} = 0.015$$

$$E = \frac{1.35 \times 10^{-5}}{7.08 \times 10^{-7} \times 0.015} = 1271 \frac{V}{m}$$

References

1. B. Sarkar and S. De, Electric field enhanced gel controlled cross-flow ultrafiltration under turbulent flow conditions, Separation and Purification Technology, 74 (2010) 73-82.
2. B. Sarkar, S. DasGupta and S. De, “Electric field enhanced fractionation of protein mixture using ultrafiltration”, Journal of Membrane Science, 341 (2009) 11-20.
3. B. Sarkar, S. DasGupta and S. De, “Flux decline during electric field assisted cross flow ultrafiltration of mosambi (Citrus sinensis (L.) Osbeck) juice” Journal of Membrane Science, 331 (2009) 75-83.
4. B. Sarkar, S. DasGupta and S. De, “Application of external electric field to enhance the permeate flux during micellar enhanced ultrafiltration” Separation and Purification Technology, 66 (2009) 263-272.
5. B. Sarkar, S. De and S. DasGupta, “Pulsed-electric field enhanced ultrafiltration of synthetic and fruit juice”, Separation and Purification Technology, 63 (2008) 582-59.

6. B. Sarkar, S. DasGupta and S. De, “Cross-flow electro-ultrafiltration of mosambi (Citrus Sinensis (L.) Osbeck) juice”, Journal of Food Engineering, 89 (2008), 241-245.
7. B. Sarkar, S. Pal, T. B. Ghosh, S. DasGupta and S. De, “A study of electric field enhanced ultrafiltration of synthetic fruit juice and optical quantification of gel deposition”, Journal of Membrane Science, 311 (2008) 112-120.
8. B. Sarkar, S. DasGupta and S. De, “Prediction of permeate flux during osmotic pressure controlled electric field enhanced cross flow ultrafiltration”, Journal of Colloid and Interface Science, 319 (2008) 236-246.
9. B. Sarkar, S. DasGupta and S. De, “Effect of electric field during gel-layer controlled ultrafiltration of synthetic and fruit juice”, Journal of Membrane Science, 307 (2) (2008) 268-276.