# Electrokinetic Effects

- Colloidal particles carry an electric charge.
- When the colloidal particles are placed in an electric field certain special effects are observed which are collectively known as electrokinetic effects.
- The electrokinetic effects are of four types depending on the movement of different phases.

*Electrophoresis,*

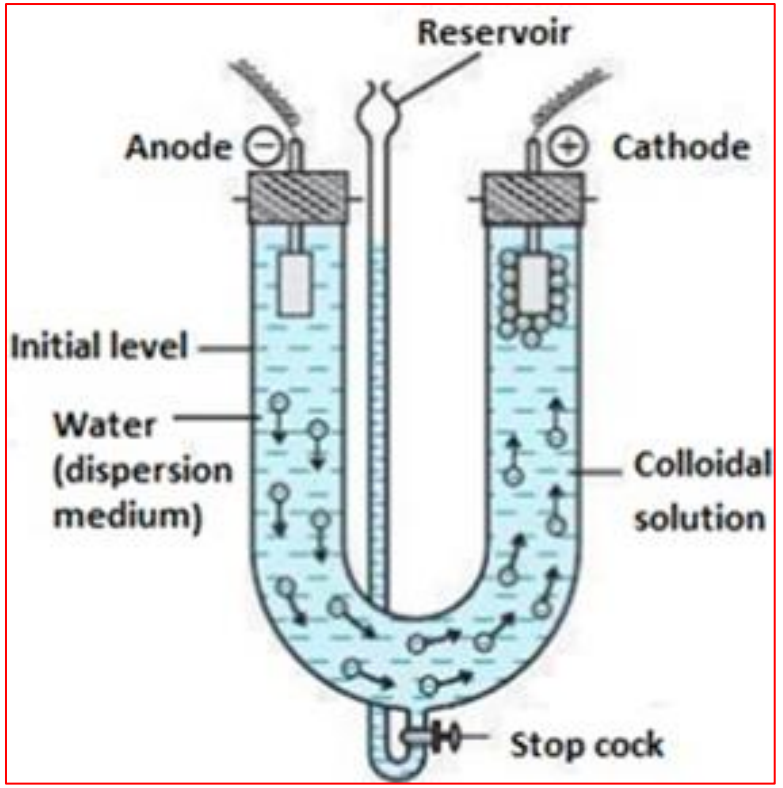
*Electcro-osmosis*

*Sstreaming potential*

*Sedimentation potential*.

# ELECTROPHORESIS

- The movement of colloidal particles in an applied electric field is known as *electrophoresis*.
- Electrophoresis is similar to electrolysis of true solutions.
- Electrophoresis can be studied by taking colloidal solution in a U tube in which two platinum electrodes are dipped. On applying a potential difference across the electrode, it is observed that the colloidal particles move to the oppositely charged electrode. Once the charged particles reaches the electrode, it gets neutralized and settle down.
- Cataphoresis - Electrophoresis of positively charged particles.
- Anaphoresis - Electrophoresis of negatively charged particles.



**Electrophoretic velocity**, $\nu_{ep}$

The velocity with which a solute moves in response to the applied electric field.

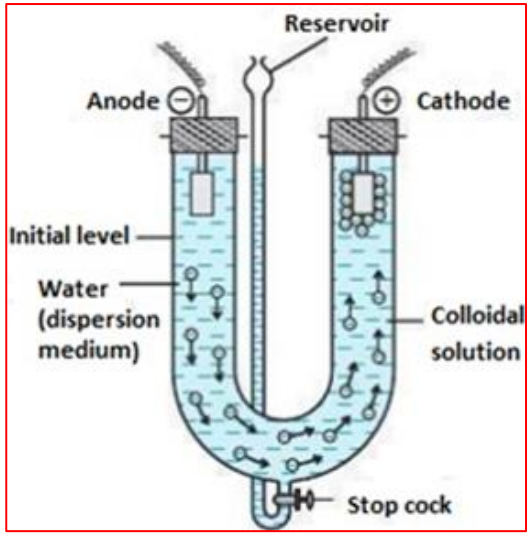
$$\nu_{ep} = \mu_{ep} E$$

$\boldsymbol{\mu_{ep}}$ is the solute's electrophoretic mobility & $\boldsymbol{E}$ is the magnitude of the applied electrical field.

$$\mu_{ep} = \frac{q}{6\pi\eta r}$$

'$q$' is the solute's charge, '$\eta$' is the buffer viscosity, and '$r$' is the solute's radius

- Electrophoretic mobility and electrophoretic velocity, increases for more highly charged solutes and for solutes of smaller size.
- Because $q$ is positive for a cation and negative for an anion, these species migrate in opposite directions.
- Neutral species, for which $q$ is zero, have an electrophoretic velocity of zero.

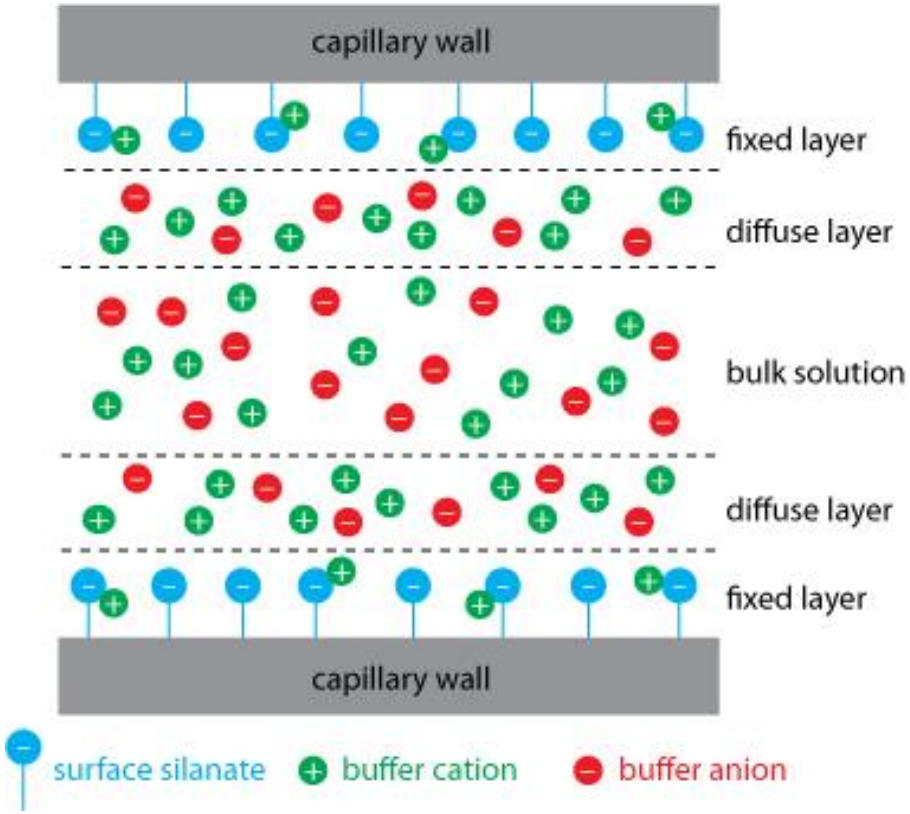


***Significance of Electrophoretic Phenomena***:

- Direction of movement of colloidal particles implies the charge on the colloidal particles.
- The phenomena is used for different applications like; for the removal of carbon from smoke, in sewage disposal, in electro-deposition *etc*..
- Electrophoresis is used in laboratories to separate macromolecules based on size.
- The technique applies a negative charge so proteins move towards a positive charge.
- Electrophoresis is used extensively in DNA, RNA and protein analysis.
- Electrophoresis is used in laboratories for the separation of molecules based on size, density and purity.

## Electro-osmosis or Electroendosmosis

- The movement of dispersion medium relative to the dispersed phase under the influence of an applied electric field.
- Electroosmotic flow occurs because the walls of the capillary tubing are electrically charged.
- The surface of a silica capillary contains large numbers of silanol groups (–SiOH).
- At pH levels greater than approximately 2 or 3, the silanol groups ionize to form negatively charged silanate ions ($–SiO^-$).
- Cations from the buffer are attracted to the silanate ions. Some of these cations bind tightly to the silanate ions, forming a fixed layer.



- Because the cations in the fixed layer only partially neutralize the negative charge on the capillary walls, the solution adjacent to the fixed layer (*ie* the diffuse layer), contains more cations than anions.
- Together these two layers are known as the double layer. Cations in the diffuse layer migrate toward the cathode. Because these cations are solvated, the solution is also pulled along, producing the electroosmotic flow.
- The rate at which the buffer moves through the capillary, what we call its **electroosmotic flow velocity**, $\nu_{eof}$, is a function of the applied electric field, *E*, and the buffer's electroosmotic mobility, $\mu_{eof}$.

$$\nu_{eof} = \mu_{eof} E$$

Electroosmotic mobility is defined as

$$\mu_{eof} = \frac{\varepsilon\zeta}{4\pi\eta}$$

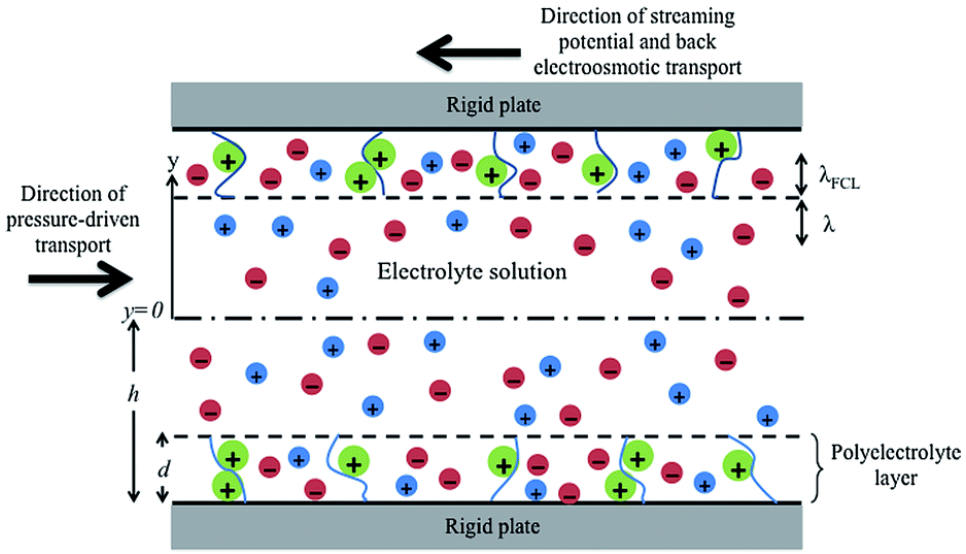
Where, '$\varepsilon$' is the buffer dielectric constant, '$\zeta$' is the zeta potential, and '$\eta$' is the buffer viscosity.

**The zeta potential :**

- The potential of the diffuse layer at a finite distance from the capillary wall—plays an important role in determining the electroosmotic flow velocity.
- Two factors determine the zeta potential’s value.
- Increasing the buffer’s ionic strength provides a higher concentration of cations, decreasing the thickness of the double layer and decreasing the electroosmotic flow.

## 3. Streaming Potential:

- **Streaming potential** originates when an electrolyte is driven by a pressure gradient through a channel or porous plug with charged walls.
- It is the reverse of electro-osmosis.
- Adjacent to the channel walls, the charge-neutrality of the liquid is violated due to the presence of the electrical double layer: a thin layer of counterions attracted by the charged surface.
- The transport of counterions along with the pressure-driven fluid flow gives rise to a net charge transport: the streaming current.
- The reverse effect, generating a fluid flow by applying a potential difference, is called electro-osmotic flow.



At steady state, the streaming potential built up across the flow system is given by:

$$U_{str} = \frac{\varepsilon_{rs}\varepsilon_0\zeta}{\eta K_L}\Delta P$$

'$\varepsilon_{rs}$' is the relative permittivity of the liquid

$\varepsilon_0$ - electrical permittivity of vacuum

η - dynamic viscosity of the liquid

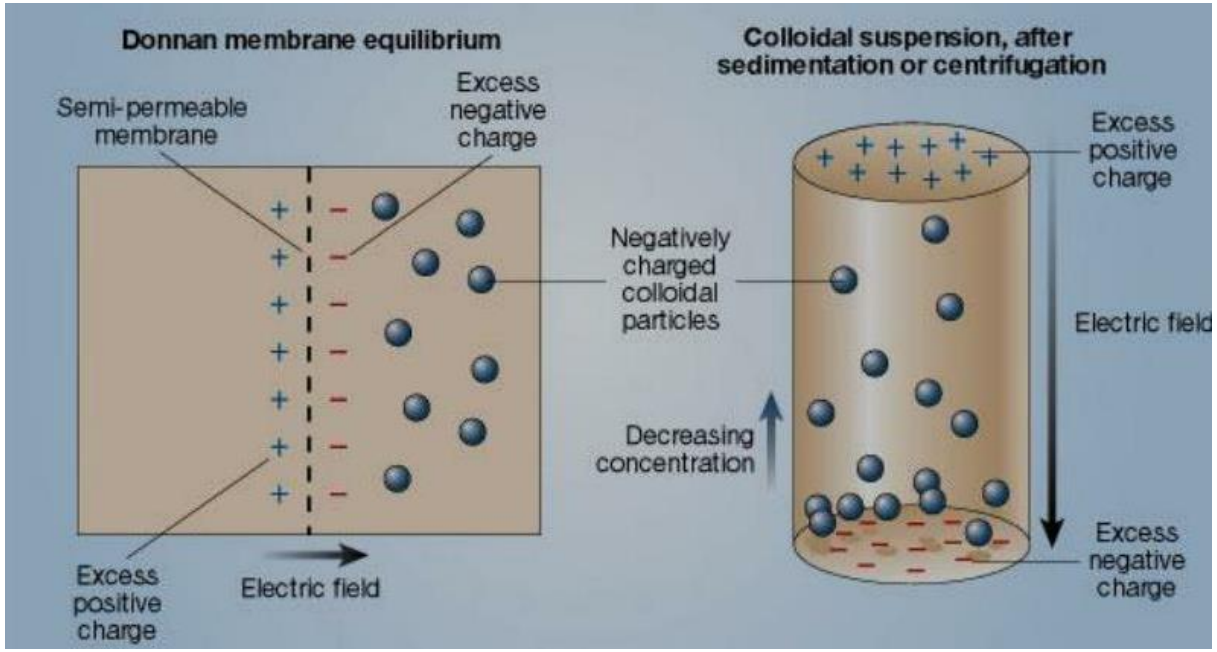
ζ - zeta potential

ΔP - pressure difference

$K_L$ - specific conductivity of the bulk liquid, $S \cdot m^{-1}$

The equation above is usually referred to as the **Helmholtz-Smoluchowski equation**.

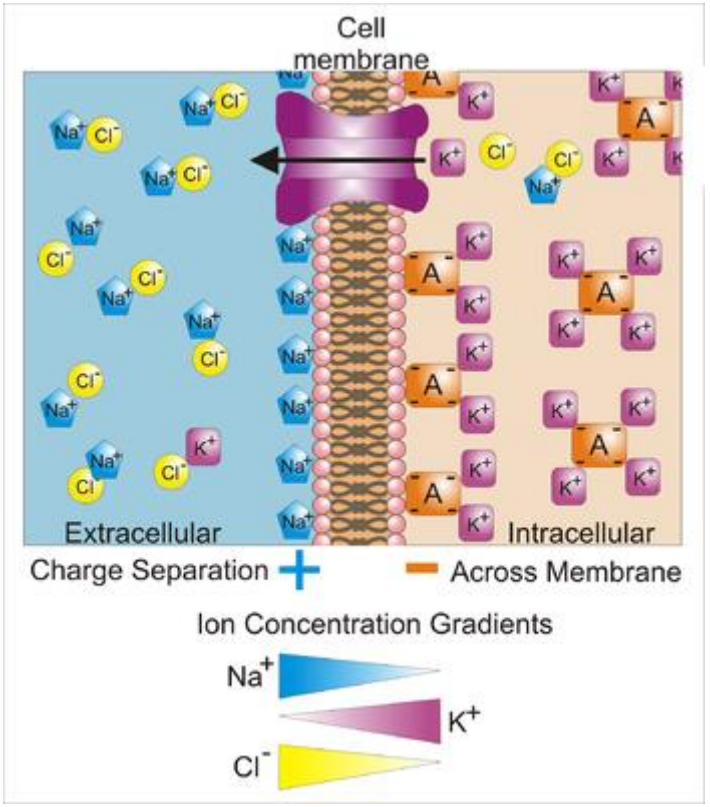
## 4. Sedimentation Potential:




- The sedimentation potential is developed in a colloidal system when particles are forced to move in a resting liquid.
- This phenomena was discovered by Dorn and hence it is also known as ***Dorn effect***.
- The movement of dispersed particles occurs under the influence of either gravity or centrifugation in a medium. This motion disrupts the equilibrium symmetry of the particle's double layer.
- While the particle moves, the ions in the electric double layer lag behind due to the liquid flow. This causes a slight displacement between the surface charge and the electric charge of the diffuse layer.
- As a result, the moving particle creates a dipole moment. The sum of all of the dipoles generates an electric field which is called *sedimentation potential*.
- It can be measured with an open electrical circuit, which is also called **sedimentation current**.

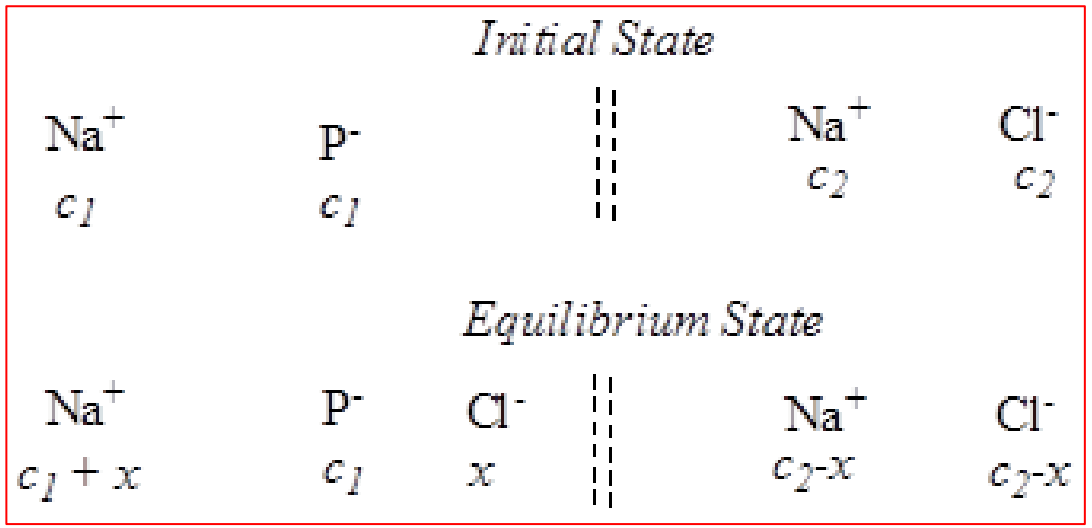
# Donnan Membrane Equilibrium

- The Donnan equilibrium describes the relation between the concentrations of the different ions in the membrane and in the adjacent electrolyte solution.
- Donnan membrane equilibrium occurs when a large, non-diffusible, charged ion is separated by a selective semi-permeable membrane.
- The large ions are usually that of macromolecules like proteins.
- This equilibrium is used to obtain the molar masses of macromlolecules by osmotic pressure method.



# *Osmotic Pressure and Concentration of Macromolecules*

- Consider a solution of sodium salt of a protein ($Na^+ P^-$) having concentration $c_1$, is separated by a semipermeable membrane from a solution of sodium chloride of concentration $c_2$.
- During osmosis the chloride ion tend to diffuse from a region of higher concentration ($c_2$) on the right to a region of lower concentration.
- However the proteins cannot cross the membrane. Inorder to maintain electrical neutrality at equilibrium, an equal number of $Na^+$ ions would also pass from right to left.
- Let '*x*' be the concentration change due to the diffusion of NaCl across the membrane.



At equilibrium, the chemical potential of NaCl on both sides of the membrane must be equal

$$\mu^0 + RT\ln\left(a_{NaCl}\right)_l = \mu^0 + RT\ln\left(a_{NaCl}\right)_r$$

Where, $a_{NaCl}$ represents the activity of NaCl, which can be represented as

$$\left(a_{NaCl}\right)_l = (a_{Na^+})_l (a_{Cl^-})_l = \left(\gamma_\pm\right)_l^2 \left[Na^+\right]_l \left[Cl^-\right]_l \quad \text{and}$$

$$\left(a_{NaCl}\right)_r = (a_{Na^+})_r (a_{Cl^-})_r = \left(\gamma_\pm\right)_r^2 \left[Na^+\right]_r \left[Cl^-\right]_r$$

Assuming that mean ionic activity coefficients on both sides are equal, then at Donnan equilibrium

$$\left[Na^+\right]_l \left[Cl^-\right]_l = \left[Na^+\right]_r \left[Cl^-\right]_r$$

Or, $(c_1+x)x = (c_2-x)\,(c_2-x) = (c_2-x)^2$

$$x = \frac{c_2^{\,2}}{c_1 + 2c_2}$$

The value of *x* depends on concentration of the salt as well as on the concentration of protein.

If the solution behaves ideally, the osmotic pressure can be calculated with the help of van't Hoff equation:

$$\Pi = RTc$$

Here *c* is the difference in molar concentrations on two sides of the membrane.

$$\Pi = 2RT\left(c_1 - c_2 + 2x\right)$$

***When concentration of the salt is small compared to the concentration of the non-diffusible ion ($c_2 <<< c_1$)***

$$\Pi = 2RT\left(c_1 + 2x\right)$$

***When concentration of the salt is large compared to the concentration of the non-diffusible ion ($c_2 >>> c_1$)***

$$x = \frac{c_2^{\,2}}{c_1 + 2c_2} = \frac{c_2^{\,2}}{2c_2} = \frac{c_2}{2} \qquad c_2 = 2x$$

$$\Pi = 2RTc_1$$

*The effect of Donnan equilibrium on osmotic pressure is eliminated by using a salt of high concentration.*