



SCH 341: SURFACE AND COLLOID CHEMISTRY NOTES

1. Adsorption of gases and vapours on solids:
 - Physical adsorption and chemisorption of gases and vapours on solids;
 - Classification of adsorption isotherms; Isotherm equations: Langmuir and BET;
2. Determination of solid surface areas;
 - Adsorption energies for physical adsorption and chemisorption;
3. Heterogeneous catalysis;
4. Surface and interfacial tensions;
 - Thermodynamics of adsorption; Gibbs equation;
5. Micelle formation monomolecular films;
 - Contact angles and wetting floatation;
 - Detergency and adsorption from solution;
6. Charge of surface, electric layer; Electrokinetics:
 - electrophoresis,
 - electro-osmosis,
 - zeta potential,
 - streaming current
 - streaming potential;
7. Colloidal state:
 - classification,
 - preparation and purification of its systems;
8. Kinetic properties;
 - Use of ultracentrifuge
 - osmotic pressure for determination of relative molecular masses of macromolecule;
9. Optical properties:
 - light scattering and macromolecular relative mass determination;
10. Rheology:
 - Phenomenon of rheology,
 - viscosity for molar mass determination;
11. Colloidal stability;
12. Coagulation and its kinetics;
13. Emulsions:
 - Types, emulsifying agents, emulsion
 - Stability and breaking emulsions;
14. Foams:
 - Stability and antifoaming agents.

SURFACE CHEMISTRY AND INTERFACE

Surface Chemistry is the study of all physico-chemical changes occurring at the interfaces of different substances, such as gases, liquids and solids.

SURFACES AND INTERFACES

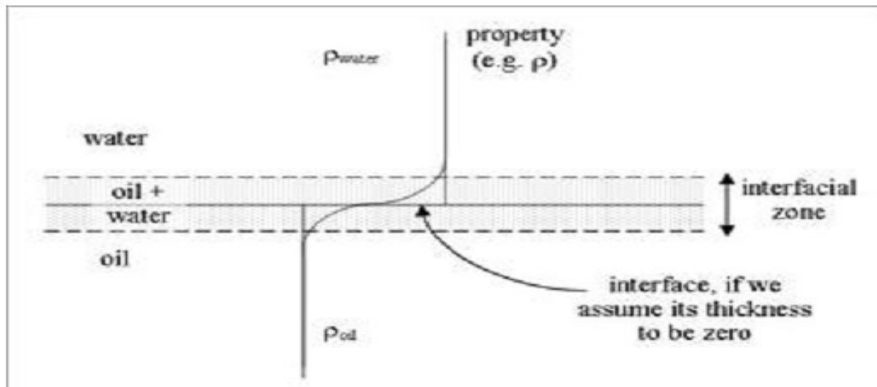
Surface:

There exist a lot of definitions among which the most rigorous ones are:

- A surface represents the outer or the topmost boundary of a solid or liquid object, where the bulk properties are no longer sufficient to describe the system's properties.
- A surface is the boundary between the 'inner' and 'outer' world of a given phase.
- A surface always determines a thermodynamic phase boundary, where the physical and chemical properties of the adjacent phases change abruptly.

Interface:

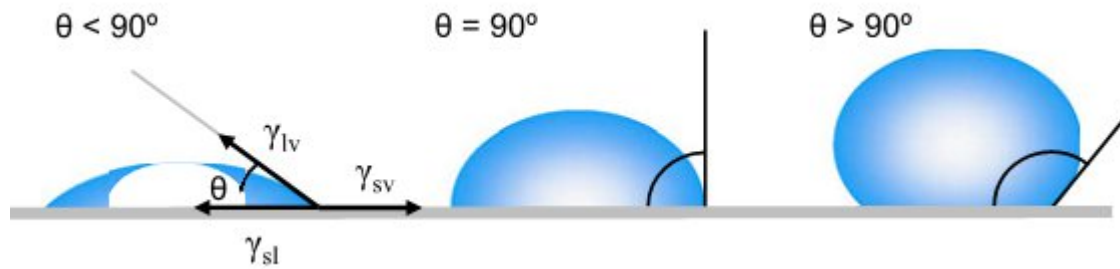
An interface is the surface of contact between any two condensed phases i.e. the surface of separation or the contact between two immiscible phases. It is not sharp in the sense that it cannot be clearly defined where a particular phase ends and the next begins. Higher the miscibility of the two phases, higher the diffusion between the two surfaces. In the interfacial zone, there is a gradual change in density. An interface is in a sense a colloid because here we have a system in the range of $1\mu\text{m}$ or smaller.



The solid-liquid interface

Contact angles and Wetting

The **contact angle** is an angle that a liquid creates with a solid surface or capillary walls of a porous material when both materials come in contact together.



This angle is determined by both properties of the solid and the liquid and the interaction and repulsion forces between liquid and solid and by the three phase interface properties (gas, liquid and solid). Those interactions are described by *cohesion and adhesion* forces which are intermolecular forces. The balance between the cohesive forces of similar molecules such as between the liquid molecules (i.e. hydrogen bonds and Van der Waals forces) and the adhesive forces between dissimilar molecules such as between the liquid and solid molecules (i.e. mechanical and electrostatic forces) will determine the contact angle created in the solid and liquid interface.

Wetting is the displacement from a surface of one fluid by another. It involves, therefore, three phases, at least two of which must be fluids. The wetting is determined by measuring the contact angle, which the liquid forms in contact with the solids or liquids.

Generally,

- If the wetting tendency is larger, then the contact angle or the surface tension is smaller.
- if the water contact angle is smaller than 90° , the solid surface is considered **hydrophilic**
- if the water contact angle is larger than 90° , the solid surface is considered **hydrophobic**. Many **polymers** exhibit hydrophobic surfaces.
- Highly hydrophobic surfaces made of low surface energy (e.g. **fluorinated**) materials may have water contact angles as high as $\sim 120^\circ$
- A wetting liquid is a liquid that forms a contact angle with the solid which is smaller than 90° .
- A non-wetting liquid creates a contact angle between 90° and 180° with the solid.

A wetting agent is a (surface-active) substance which promotes this effect. Three types of wetting can be distinguished:

- Spreading wetting.
- Adhensional wetting.
- Immersional wetting.

a) Spreading wetting: In this, a liquid already in contact with the solid spreads so as to increase the solid-liquid (SL) and liquid-gas (LG) interfacial areas and decrease the solid-gas interfacial area. The spreading coefficient, S (equation below), is defined by the expression;

$$S = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG})$$

- The liquid spreads spontaneously over the solid surface when S is positive or zero.
- When S is negative, the liquid remains as a drop having a definite angle of contact, θ , with the solid surface.

Example

Given the following data on interfacial tensions (mN/m) (note: VA = valeric acid) [12 marks]

Interface	$\gamma/(\text{mNm}^{-1})$	Interface	$\gamma/(\text{mNm}^{-1})$
air/water	72	Hg/water	415
air/VA	25	Hg/VA	329
air/hexane	18	Hg/hexane	378
air/Hg	485	hexane/H ₂ O	50

- Will hexane spread at the air/water surface?
- Will hexane spread at the air/Hg surface?
- Will hexane spread at the Hg/water interface?
- Will VA spread at the Hg/H₂O interface?

i)

$$S = \gamma_{\text{Air/H}_2\text{O}} - (\gamma_{\text{Air/Hex}} + \gamma_{\text{Hex/H}_2\text{O}}) = (72 - \{18 + 50\}) \frac{\text{mN}}{\text{m}}$$

$$= 4 \frac{\text{mN}}{\text{m}} \Rightarrow \text{spontaneous spreading}$$

ii)

$$S = \gamma_{\text{Hg}} - (\gamma_{\text{Hex/Hg}} + \gamma_{\text{Hex}}) = (485 - \{378 + 18\}) \frac{\text{mN}}{\text{m}}$$

$$= 89 \frac{\text{mN}}{\text{m}} \Rightarrow \text{spontaneous spreading}$$

iii)

$$S = \gamma_{\text{Hg/H}_2\text{O}} - (\gamma_{\text{Hex/Hg}} + \gamma_{\text{Hex/H}_2\text{O}}) = (415 - \{378 + 50\}) \frac{\text{mN}}{\text{m}}$$

$$= -13 \frac{\text{mN}}{\text{m}} \Rightarrow \text{non - spontaneous spreading}$$

iv)

$$S = \gamma_{\text{Hg/H}_2\text{O}} - (\gamma_{\text{VA/Hg}} + \gamma_{\text{VA/H}_2\text{O}}) = (415 - \{329 + 53\}) \frac{\text{mN}}{\text{m}}$$

$$= 33 \frac{\text{mN}}{\text{m}} \Rightarrow \text{spontaneous spreading}$$

Adhensional wetting: In this, a liquid which is not originally in contact with the solid substrate makes contact and adheres to it. In contrast to spreading wetting, the area of liquid-gas interface decreases. The work (free energy) of adhesion is given by the Dupre" equation in the form;

$$W_a = -\Delta G_a / A$$

$$= \gamma_{SG} + \gamma_{LG} - \gamma_{SL}$$

Immersional wetting: Here, the solid, which is not originally in contact with the liquid, is immersed completely in the liquid. The area of liquid-gas interface, therefore, remains unchanged. The free energy change for immersion of a solid in a liquid is given by:

$$-\Delta G_i = \gamma_{SG} - \gamma_{SL}$$

$$= \gamma_{LG} \cos \theta$$

If $\gamma_{SG} > \gamma_{SL}$, then $0 < 90^\circ$ and immersional wetting is spontaneous, but if $\gamma_{SG} < \gamma_{SL}$, then $0 > 90^\circ$ and work must be done to immerse the solid in the liquid.

Adsorption and Types of Adsorption

Adsorption

Due to unbalanced attraction forces, accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed as adsorption.

Adsorbate: The molecular species or substance which accumulate at the surface.

Adsorbent: -The surface of material on which Adsorption takes place. , e.g

- (i) O₂, H₂, Cl₂ gases are adsorbed on the surface of charcoal.
- (ii) Silica gels adsorb water molecules from air.

Charcoal, silica gel, metals such as Ni, Cu, Ag, Pt and colloids are some adsorbents.

Desorption: The process of removing of adsorbed substance from the surface on which it is adsorbed.

Absorption: -When the molecular species or substance enters in the bulk phase in solid or liquid is called as Absorption.

Sorption: - When both adsorption and absorption takes place simultaneously is called as sorption process.

Difference between adsorption and absorption

Adsorption	Absorption
<ul style="list-style-type: none"> • Involves unequal distribution of the molecular species in bulk and at the surface. • It is a surface phenomenon. • It is rapid in the beginning. 	<ul style="list-style-type: none"> • Involves unequal distribution of the molecular species in bulk and at the surface. • It occurs throughout the body of the material. • It occurs at a uniform rate.

Important Characteristics of Adsorption

1. It is specific and selective in nature.
2. Adsorption is spontaneous process, therefore change in free energy (ΔG) is negative.

$\Delta G = \Delta H - T\Delta S$, For the negative value of ΔG , in a system, in which randomness decreases, ΔH must be negative.

Hence, adsorption is always exothermic.

NB: Adsorption of hydrogen over Pt is called occlusion.

Positive and Negative Adsorption

When the concentration of the adsorbate is more on the surface of the adsorbent than in the bulk, it is called positive adsorption. On the other hand, if the concentration of the adsorbate is less relative to its concentration in the bulk, it is called negative adsorption, e.g., when a dilute solution of KCl is shaken with blood charcoal, it shows negative adsorption.

Mechanism of Adsorption

Inside the Adsorbent (in bulk) the force acting between the particles are mutually balanced but on the surface, the particles are not surrounded by atoms or molecules of their kind on all sides and hence they possess attraction force so particles stick on the surface of the Adsorbent.

The extent of adsorption increases with increase in surface area per unit mass of the adsorbent at a given temperature and pressure.

Types of adsorption

Depending on the type of forces that hold the adsorbed molecules on the surface has a considerable effect on certain characteristics. Thus adsorption can be divided into two types.

There are two types of adsorption

i. Physical (van der waals) Adsorption or physisorption: - If accumulation of gas on the surface of solid occurs on account of weak vanderwaals forces is called physical Adsorption. **Examples;** Adsorption of hydrogen or oxygen on charcoal or adsorption of nitrogen on mica.

On physical adsorption, individual molecules of adsorbate remain attached to the surface of adsorbent for a short time and then they get desorbed. The desorption process has a rate constant k_d

$$k_d = Ae^{E_a/RT}$$

Where

- A= Proportionality constant
- E_a = Activation energy for the desorption process.
- T =Temperature
- R= 8.314Jmol⁻¹k⁻¹

The reciprocal of the desorption rate constant is called the mean or average life time γ for the adsorbed molecule.

The reciprocal of A is given as γ_0 . Therefore;

$$\gamma = \gamma_0 e^{E_a/RT}$$

$$\ln\left(\frac{\gamma}{\gamma_0}\right) = E_a/RT$$

Example: calculate the mean life time of adsorbate molecule for an adsorbent surface at 300k if the desorption activation energy for the system is;

- i. 20kJmol⁻¹
- ii. 200kJmol⁻¹

(Assume $\gamma_0 = 10^{-10}$, R= 8.314Jmol⁻¹k⁻¹)

solution

$$i. \ln\left(\frac{\gamma}{10^{-10}}\right) = 20000/R \times 300$$

$$\gamma = 3.03 \times 10^{-7} \text{ seconds}$$

$$\text{ii. } \ln \left(\frac{r}{10^{-10}} \right) = 200000/R \times 300$$

$$r = 6.58 \times 10^{24} \text{ seconds}$$

ii. Chemical Adsorption or chemisorption: - When gas molecules or atoms are held to the surface (solid) by chemical bonds, the Adsorption is called Chemical Adsorption.

Differentiation between Physical and Chemical Adsorption

Chemisorptions

1. Heat of adsorption is greater than 80 kilo joules per mole.
2. This adsorption mostly occurs at high temperature.
3. Chemisorption is highly specific.
4. It depends both on adsorbate and adsorbant.
5. It is irreversible in nature.
6. Chemisorption decreases with the increase of pressure of the adsorbate.

Physisorption

1. Heat of adsorption is less than 40 kilo joules per mole.
2. This adsorption mostly occurs at low temperature.
3. Physical adsorption is not specific.
4. It depends only on the adsorbate.
5. It is reversible in nature.
6. The extent of physical adsorption increases with increase of pressure of the adsorbate.

Factors Affecting Adsorption

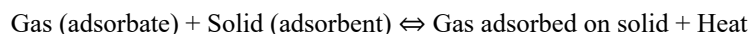
(a) Nature of adsorbent : Same gas may be adsorbed to different extents on different adsorbent.

(b) Surface area of the adsorbent: Greater the surface area, greater is the extent of adsorption.

(c) Nature of the gas being adsorbed: Greater is the critical temperature of a gas, greater are the van der Waals' forces of attraction and thus, greater is the adsorption.

Gas	H ₂	N ₂	CO	CH ₄	CO ₂	HCl	NH ₃	SO ₂
Critical temp (K)	33	126	134	190	304	324	406	430

(d) Temperature: Adsorption is an exothermic process involving the equilibrium :



Applying Le-Chatelier principle, increase of temperature decreases the adsorption and vice-versa.

This can be fitted into the equation;

$$\text{Log } \frac{V_2}{V_1} = - \frac{\Delta H}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = - \frac{\Delta H}{2.303R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

Where V₁ and V₂ are gas volumes adsorbed at constant pressure and at T₁ and T₂.

Example; on one gram of charcoal and a gas pressure of 1 atm, volume of N₂ adsorbed at 88k is 155cm³ and at 273k is 15cm³. Calculate heat of adsorption of N₂ on charcoal. (R= 8.314Jmol⁻¹k⁻¹).

Solution

$$\Delta H = - \left(\frac{2.303R T_1 T_2}{T_1 - T_2} \right) \text{Log } \frac{V_2}{V_1}$$

$$\Delta H = - \left(\frac{2.303 \times 8.314 \times 88 \times 273}{(88 - 273)} \right) \text{Log } \frac{15}{155}$$

$$= -2522 \text{Jmol}^{-1}$$

(e) **Pressure:** Adsorption increases with pressure at constant temperature. The effect is large if temperature is kept constant at low value.

(f) **Activation of the solid adsorbent :** Activation means increasing the adsorbing power of the solid adsorbent. This can be done by subdividing the solid adsorbent or by removing the gases already adsorbed by passing superheated steam.

Adsorption Isotherms

The adsorption of a gas or vapours on a solid surface in a closed vessel is a reversible process and depends on pressure and temperature.

The process of Adsorption is usually studied through graphs known as **adsorption isotherm**. It is the graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature.

Different adsorption isotherm theories are;

- i. Freundlich,
- ii. Langmuir
- iii. BET theory.

a). Langmuir Adsorption Isotherm

Irving Langmuir derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

$$\theta = \frac{KP}{1 + KP}$$

Where

- θ = the number of sites of the surface which are covered with gaseous molecule,
- P = pressure
- K = the equilibrium constant for distribution of adsorbate between the surface and the gas phase.

At lower pressure, KP is so small, that factor (1+KP) in denominator can almost be ignored. So Langmuir equation reduces to: $\theta = KP$

At high pressure KP is so large, that factor (1+KP) in denominator is nearly equal to KP. So Langmuir equation reduces to



Derivation of the Langmuir Adsorption Equation

Let θ the number of sites of the surface which are covered with gaseous molecules.

Therefore, the fraction of surface which are unoccupied by gaseous molecules will be (1 - θ).

Rate of forward direction depends upon two factors:

- i. Number of sites available on the surface of adsorbent, (1 - θ).
- ii. Pressure, P.

Therefore rate of forward reaction is directly proportional to both mentioned factors.

$$\text{Rate of forward reaction} \propto P(1-\theta)$$

$$\text{Rate of adsorption} \propto P(1-\theta)$$

$$\text{Rate of adsorption} = K_a P(1-\theta)$$

Similarly, Rate of backward reaction or Rate of Desorption depends upon number of sites occupied by the gaseous molecules on the surface of adsorbent.

$$\text{Rate of desorption} \propto \theta$$

$$\text{Rate of desorption} = K_d \theta$$

At equilibrium, rate of adsorption is equal to rate of desorption.

$$K_a P (1 - \theta) = K_d \theta$$

We can solve the above equation to write it in terms of θ .

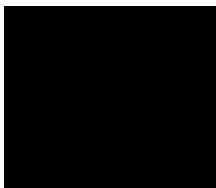
$$K_a P - K_a P \theta = K_d \theta$$

$$K_a P = K_a P \theta + K_d \theta$$

$$K_a P = (K_d + K_a P) \theta$$



Divide numerator and denominator on RHS by K_d , we get



Now put



In above equation we get

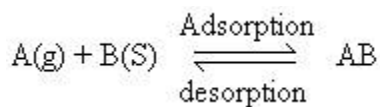


This is known as Langmuir Adsorption Equation.

Assumptions of Langmuir Isotherm

Langmuir proposed his theory by making following assumptions.

1. Fixed number of vacant or adsorption sites are available on the surface of solid.
2. All the vacant sites are of equal size and shape on the surface of adsorbent.
3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process.
4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.



Where A (g) is unadsorbed gaseous molecule, B(s) is unoccupied metal surface and AB is Adsorbed gaseous molecule.

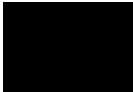
5. Adsorption is monolayer or unilayer.

Alternate form of Langmuir Adsorption Equation

Langmuir adsorption equation can be written in an alternate form in terms of volume of gas adsorbed.

Let

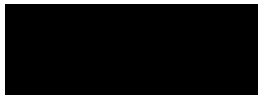
- V be volume of gas adsorbed under given sets of conditions of temperature and pressure
- V_{mono} be the adsorbed volume of gas at high pressure conditions so as to cover the surface with a unilayer of gaseous molecules.

Substituting  the value of θ in Langmuir equation

$$\frac{V}{V_{mono}} = \frac{KP}{1 + KP}$$

$$\text{Or } V_{mono} = 1 + \frac{1}{KP}$$

Or in terms of pressure P we get,



Langmuir Adsorption Equation in alternate form

Thus, if we plot a graph between P/V Vs P, we will obtain a straight line with

$$\text{slope} = \frac{1}{V_{mono}} \quad \text{and} \quad \text{Intercept} = \frac{1}{KV_{mono}}$$

This value of V_{mono} can be used to form an estimate of surface area of an adsorbent if molecular diameter of the adsorbed gas is known.

Surface area of an adsorbent

In adsorption systems where Langmuir’s model is followed, the maximum amount of adsorbate adsorbed per gram of adsorbent for the formation of monolayer, X_m (mg/g), is determined. Knowing the approximate contact area of an adsorbate molecule, surface area of adsorbent could be calculated using following equation:

$$\text{Surface area of the adsorbent (m}^2\text{/g)} = \frac{X_m(\text{mg/g}) \times N \times S(\text{m}^2 \text{ / molecule})}{M}$$

Here,

- X_m = Maximum amount of adsorbate adsorbed per gram of adsorbent for monolayer formation,
- M = Molecular weight of the adsorbate (mg/molecule),
- N = Avogadro’s number
- S = Contact surface area by each molecules (m^2).

Example 1:

The volume of nitrogen gas at 1 atm and 273K required to cover 1g of the silica gel is 0.129 dm³. Calculate the surface area of the gel if each nitrogen molecule occupies an area of 16.2 X 10⁻²⁰ m²

Solution:

Number of moles of N₂ in 0.129dm³

$$= 0.129/22.4 = 5.76 \times 10^{-3} \text{ moles of } N_2 \text{ gas}$$

Therefore, total number of N₂ molecules in 0.129 dm³ of N₂

$$= 5.76 \times 10^{-3} \times 6.02 \times 10^{23} \text{ molecules} / 22.4 \text{ dm}^3 \\ = 34.67 \times 10^{20}$$

The total area of 1g of the silica gel = 34.67 x 10²⁰ x 16.2 x 10⁻²⁰m²

$$= 561.74 \text{ m}^2$$

Question 2: The volume of hydrogen gas at 1 atm and 273K required to cover 1g of the silica gel is 0.127dm³.

Identify the area occupied by the silica gel in each hydrogen molecule in which the molecule occupies an area of 17.3 ×10⁻²⁰ m².

Solution:

Number of moles of H₂ in 0.127dm³ = 0.127/22.4 = 5.66 ×10⁻³

Therefore, total number of H₂ = 5.66 ×10⁻³ × 6.02 ×10²³

Total number of H₂ = 34.13 ×10²⁰

The total area of 1g of the silica gel = 34.13 ×10²⁰ × 17.3 ×10⁻²⁰

The total area of 1g of the silica gel = 590.449 m²

Alternatively molecular diameters may be estimated from **Langmuir isotherm**, if the adsorbing surface area (smooth and polished) area is known.

Example 3; In adsorption of hydrogen over a sample of copper, monolayer formation volume per gram of powder was found to be 1.36 ml measured at stp. Calculate the specific surface area of copper. Liquid hydrogen has a density of 0.07g/cm³.

solution

For 1.36 cm³ of H₂ at stp,

The number of molecules = $\frac{1.36 \text{ cm}^3}{22400 \text{ cm}^3} \times 6.0 \times 10^{23} \text{ molecules}$

$$= 3.6 \times 10^{19} \text{ molecules}$$

In liquid hydrogen, its molecules can be regarded as close packed. This information can be used to calculate the cross sectional area of one molecule.

$$\text{Volume of one molecule} = \frac{2}{0.07 \times 6.0 \times 10^{23}}$$

$$47.62 \times 10^{-24} \text{ cm}^3$$

Therefore molecular radius r can be calculated

$$4/3 \pi r^3 = 47.62 \times 10^{-24}$$

$$r^3 = \frac{3 \times 47.62}{4 \times 3.14} \times 10^{-24}$$

$$r = 2.25 \times 10^{-8} \text{ cm}$$

Cross sectional area of the molecule,

$$\pi r^2 = (2.25)^2 \times 10^{-16} = 15.91 \times 10^{-16} \text{ cm}^2$$

Surface area per gram of copper powder

$$3.6 \times 10^{19} \text{ molecules} \times 15.91 \times 10^{-16} \text{ cm}^2$$

$$= 5.73 \times 10^4 \text{ cm}^2$$

Limitations of Langmuir Adsorption Equation

1. **Langmuir Equation is valid under low pressure only.**
2. Langmuir Equation assumes that adsorption is monolayer. But, monolayer formation is possible only under low pressure condition. Under high pressure condition the assumption breaks down as gas molecules attract more and more molecules towards each other.
3. Another assumption was that all the sites on the solid surface are equal in size and shape and have equal affinity for adsorbate molecules i.e. the surface of solid is homogeneous. But we all know that in real solid surfaces are heterogeneous.
4. **Langmuir Equation assumed that molecules do not interact with each other.** This is impossible as weak force of attraction exists even between molecules of same type.
5. The adsorbed molecules has to be localized i.e. decrease in randomness is zero ($\Delta S = 0$). This is not possible because on adsorption liquefaction of gases taking place, which results into decrease in randomness but the value is not zero.

From above facts we can conclude that, Langmuir equation is valid under low pressure conditions.

Application of Langmuir adsorption isotherm

- i. The Langmuir adsorption isotherm gives a quantitative explanation of the adsorption.
- ii. The mechanism of chemical adsorption can be explained with the help of Langmuir equation.
- iii. The Langmuir adsorption isotherm gives a satisfactory theoretical explanation of a large number of experimental results.

(b) The Freundlich adsorption isotherm

Freundlich described the variation of the amount of the gas adsorbed per unit mass of the adsorbent with pressure at constant temperature by means of the relationship;



Where;

- **x** is the mass of the gas adsorbed on mass **m** of the adsorbent at pressure **p**,
- **k, n** are constants whose values depend upon adsorbent and gas at particular temperature.

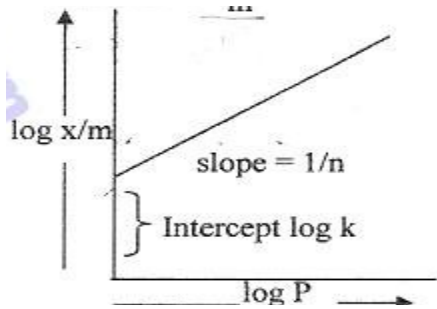
Though Freundlich Isotherm correctly established the relationship of adsorption with pressure at lower values, it failed to predict value of adsorption at higher pressure.

Taking logs on both sides;

$$\log \frac{x}{m} = \log K p^{1/n}$$

$$\log \frac{x}{m} = \log K + 1/n \log p$$

This is an equation of a straight line. Hence a plot of $\log \frac{x}{m}$ against $\log p$ should be a straight line with slope equal to $1/n$ and intercept equal to $\log k$ as shown below.



Question: Charcoal absorbs a solute from its aqueous solution and obeys the Freundlich isotherm. The following were the data obtained.

Equilibrium concentration
x

$10^2 M$	2.0	4.0	6.0	8.0
x/m	0.18	0.29	0.36	0.42
	5	0	4	8

Determine the values of K. ($n = 0.616$).

Solution:

$$X_m = K P^{1/n}$$

$$0.3155 = K (10)(0.616)$$

$$0.3155 = K (6.16)$$

$$K = 0.31556.16$$

$$K = 0.05121 \times 10^2 M$$

$$K = 5.12 M.$$

Also the Freundlich Adsorption Isotherm equation can be expressed as,

$$q = K_d C^{(1/n)}$$

Where,

q = the amount of adsorption,

C = Equilibrium concentration of the adsorptive,

K_d = distribution coefficient,

n = correction factor.

This model shows the relationship between the concentration of a solute on the surface of an adsorbent and the concentration of the solute in the liquid.

Question 1: Calculate the amount of adsorption using Freundlich isotherm of the solute on activated charcoal in which the Slope value $n = 0.2$ and the distribution coefficient is $k = 0.19$. The equilibrium concentration of the adsorptive is 0.12.

Solution:

Given data,

$$n = 0.2$$

$$K_d = 0.19$$

$$C = 0.12$$

Substitute the values in the corresponding equation

$$q = K_d C^{(1/n)}$$

$$q = (0.19) (0.12)^{(1/0.2)}$$

$$q = 0.124.$$

Question 2: Calculate the adsorption of a dye on activated carbon at 25°C, where $k = 0.025$, $n = 0.5$ and $C = 0.04$.

Solution:

Given data

$$n = 0.5$$

$$K_d = 0.025$$

$$C = 0.04$$

Substitute the values in the corresponding equation

$$q = K_d C^{(1/n)}$$

$$q = (0.025) (0.04)^{(1/0.5)}$$

$$q = 0.040.$$

Applications of Freundlich adsorption isotherm

- i. The Freundlich adsorption log isotherm is used to determine the extent of adsorption of gases by solids at low pressures.
- ii. used for the adsorption of a solute in a solution, when the pressure is replaced by the concentration “C” of the solute.

Limitations of Freundlich adsorption isotherm

- 1) Freundlich adsorption isotherm is approximate and cannot be regarded as an equation of general applicability.
- 2) This adsorption isotherm is valid over a certain range of pressure only.
- 3) The values of constant “K” and “n” vary with temperature

c) BET adsorption Isotherm

BET (Brunauer, Emmett and Teller) equation is used to give specific surface area from the adsorption data. The BET equation is used to give the volume of gas needed to form a monolayer on the surface of the sample. The actual surface area can be calculated from knowledge of the size and the number of the adsorbed gas molecules. Nitrogen is used most often to measure BET surface, but if the surface area is very low, argon or krypton may be used as both give a more sensitive measurement, because of their lower saturation vapor pressures at liquid nitrogen temperature.

BET equation is as follows:

$$\frac{z}{(1-z)} \cdot \frac{1}{V} = \frac{(c-1)z}{cV_{mono}} + \frac{1}{cV_{mono}}$$

Where,

- V = volume of gas adsorbed at pressure p;
- V_m = amount of gas corresponding to one monolayer;
- z = p/p*, ratio of pressure of gas and pressure at saturation;
- c = a constant.

A plot of z/(1-z)V vs z gives slope (c-1)/cV_{mono} and intercept at z = 0 , and cV_{mono} could be determined. The results can be combined to give c and V_{mono}.

When the coefficient c is large, the isotherm takes the simpler form as follows.

$$\frac{V}{V_{mono}} = \frac{1}{1-z}$$

This is applicable to unreactive gases on polar surfaces, for their c is approx. 10². Higher value of c will mean mainly monolayer formation. The value of V_{mono}, the volume of gas required to form monolayer, is of considerable interest because it helps in the calculation of surface area of a porous solid. The surface area occupied by a single molecule of adsorbate on the surface can be calculated from the density of the liquefied adsorbate.

For example, the area occupied by a nitrogen molecule at -195° C estimated to be 16.2 x10⁻²⁰ m² assuming molecules to be spherical and close packed in the liquid. Thus, from the value of V_{mono} obtained from the BET theory, surface area of the adsorbent could be determined.

Example: The data given below are for the adsorption of nitrogen on alumina at 77.3 K. Show that they fit in a BET isotherm in the range of adsorption and find V_{mono} and hence surface area of alumina (m²/g). At 77.3 K, saturation

pressure, $P^* = 733.59$ torr. The volumes are corrected to STP and refer to 1g of alumina.

P/ (torr)	37.67	74.20	114.54	142.0	185.34
V (cm ³ /g: STP)	23.14	28.1	33.1	36.35	41.49

Solution:

From the above data, we have

$10 \times Z = 10 \times (P/P^*)$	0.51	1.01	1.56	1.94	2.53
$x = 10^3 Z/(1-Z) (V/cm^3)$	2.32	3.99	5.58	6.62	8.16

From BET equation, $\frac{z}{(1-z)} \cdot \frac{1}{V} = \frac{(c-1)z}{cV_{\text{mono}}} + \frac{1}{cV_{\text{mono}}}$

A plot of $z/(1-z)$ against z will give a straight line with intercept $z = 0$ as equal to $\frac{1}{cV_{\text{mono}}}$ and slope will be

$$\frac{(c-1)}{cV_{\text{mono}}}$$

Intercept of the plot is $0.987 \times 10^{-3} \text{ cm}^{-3}$ where as slope = $2.88 \times 10^{-2} \text{ cm}^{-3}$

$$\text{Intercept} = \frac{1}{cV_{\text{mono}}} = 0.987 \times 10^{-3} \text{ cm}^{-3} = 9.87 \times 10^{-4} \text{ cm}^{-3}$$

$$\text{Slope} = \frac{(c-1)}{cV_{\text{mono}}} = 2.88 \times 10^{-2} \text{ cm}^{-3}$$

$$2.88 \times 10^{-2} \text{ cm}^{-3} = (C-1) \times \frac{1}{cV_{\text{mono}}}$$

$$= (C-1) \times 9.87 \times 10^{-4} \text{ cm}^{-3}$$

$$(C-1) = 2.88 \times 10^{-2} / 9.87 \times 10^{-4} = 29.18$$

$$C = 30.18$$

$$\text{Further, } \frac{1}{cV_{\text{mono}}} = 9.87 \times 10^{-4} \text{ cm}^{-3}$$

$$V_{\text{mono}} = 1 / C \times 9.87 \times 10^{-4} \text{ cm}^{-3}$$

$$= 1 / 30.18 \times 9.87 \times 10^{-4}$$

$$= 33.57 \text{ cm}^3$$

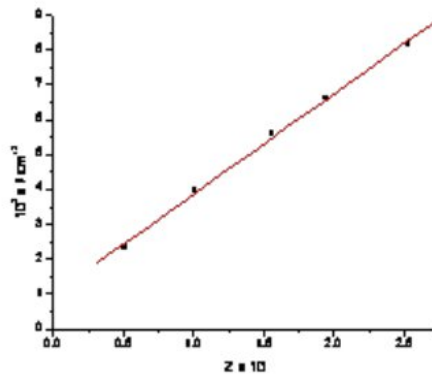
$$= 0.03357 \text{ dm}^3$$

$$\text{Number of } N_2 \text{ molecules} = (0.03357/22.4) \times 6.02 \times 10^{23}$$

$$= 9.022 \times 10^{20} \text{ molecules}$$

$$\text{The total area} = 9.022 \times 10^{20} \times 16.2 \times 10^{-20} \text{ m}^2$$

$$= 146.156 \text{ m}^2/\text{g} \text{ (contact area of one } N_2 \text{ molecule} = 16.2 \times 10^{-20} \text{ m}^2 \text{)}$$



Catalysis

- The phenomenon where the rate of a chemical reaction is altered (change) by a substance which remains unchanged after the reaction.

Berzelius catalyst:

- Substance which alter (change) the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction are known as **catalyst** and the phenomenon is known as catalysis.

Promoter: - substance that enhance (increase) the activity of catalyst.

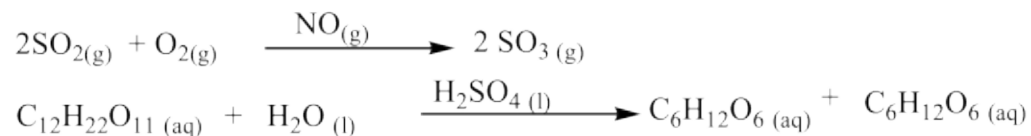
Poisons: - it decreases the activity of catalyst.

A catalyst may be positive (i.e., increases rate of reaction) or negative (i.e., decreases rate of reaction).

Types of Catalysis

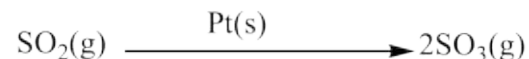
a) Homogeneous Catalysis: - When the reactants and the catalyst are in the same phase (i.e. liquid or gas).

Examples: -



b) Heterogeneous catalysis: The catalytic process in which the reactant and the catalyst are in different phase is known as heterogeneous catalysis.

Example: -



Adsorption Theory of Heterogeneous Catalysis

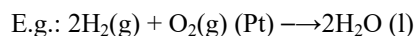
The mechanism involves five steps:

- (i) Diffusion of reactants to the surface of the catalyst
- (ii) Adsorption of reactant molecules on the surface of the catalyst.
- (iii) Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate.
- (iv) Desorption of reaction products from the catalyst surface.
- (v) Diffusion of reaction products away from the catalyst's surface

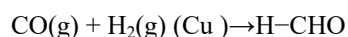
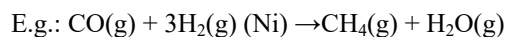
(c) Autocatalysis: When one of the product of a reaction acts as catalyst, the process is called autocatalysis.

Important Features of Solid Catalysts

i) Activity: The activity (efficiency) of a solid catalyst depends on how strongly the reactants are chemisorbed on it. It is found that elements (metals) in group 7-9 of the periodic table show greater catalytic activity for hydrogenation reactions.



ii) Selectivity: For a given set of reactants, different catalyst may yield different products. This is selectivity of a catalyst.



Ni is selective to convert water gas to CH₄ whereas Cu converts water gas into formaldehyde. In other words Ni catalyses the conversion of water gas to CH₄ but cannot catalyse to convert water gas to formaldehyde.

Catalyst is highly selective in nature i.e a given substance can act as a catalyst only in a particular reaction and not for all the reactions.

(iii) Shape-selective catalysis; The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis.

Shape Selectivity catalysis by Zeolite

Shape Selectivity catalysis - is the catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules.

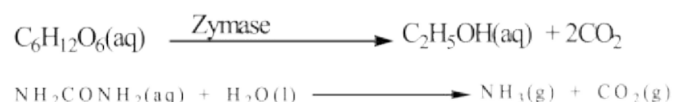
Zeolites: They are micro porous aluminosilicates with three dimensional networks of silicates in which some silicon atoms is replaced by aluminium atoms giving AL-O-Si framework.

An important Zeolite catalyst used in petroleum industry is ZSM-S.

ZSM-S converts directly Alcohols into Gasoline (Petrol) by dehydrating them to give a mixture of hydrocarbons.

Biochemical Catalysts (enzyme): - are complex nitrogenous organic compound which are produced by living plants and animals.

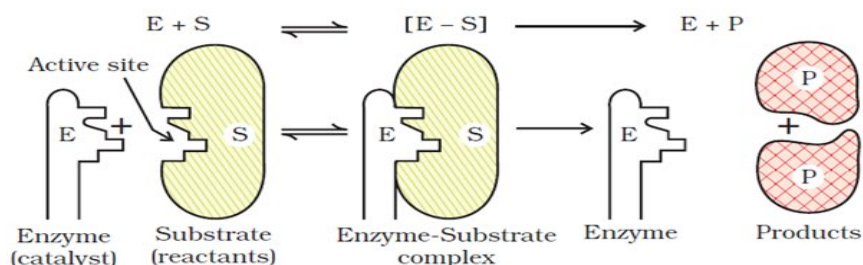
Example: -



Characteristics of Enzyme Catalysis

- Most highly efficient:* - One molecule of enzyme may transform one million molecule of reactant per minute.
- Highly specific nature:* - Each enzyme is specific for a given reaction.
- Highly active under optimum temperature:* - The rate of an enzyme reaction is maximum at definite temperature called optimum temperature (298K-310K).
- Highly active under optimum PH :-* Rate of enzyme reaction is maximum at optimum PH (5-7)
- Increasing activity in presence of activators and co-enzymes:-* The enzymatic activity in presence of certain substance called co-enzymes (vitamins) and activators are generally Na⁺, CO²⁺, Mn²⁺, Cu²⁺, etc.
- Inhibitors and poisons decrease or stop the rate of enzyme reaction.*

Mechanism of Enzyme Catalysis



There are number of cavities present on the surface of colloidal particles of enzymes. the molecules of the reactant (substrate), which have complementary shape, fit into these cavities just like a key fits into a lock. on the account of the presence of active groups. an Activated complex is formed which then decompose as to yield the products.

APPLICATIONS OF ADSORPTION

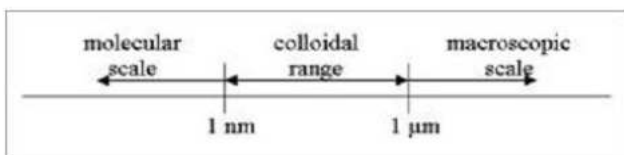
Some of the important applications of adsorption are;

1. The industrial processes like synthesis of ammonia, ethyl alcohol, manufacture of H₂SO₄ etc. involve the adsorption of the reaction on the surface of the solid catalysts.
2. Softening of hard water by ion exchange method is based on adsorption of cations.
3. Removable of colouring materials from various types of solutions by charcoal involve adsorption.
4. Most of the drugs function through adsorption on body tissues.
5. Tanning of hides, dyeing of fabrics etc. involves adsorption.
6. The lubricant action of graphite is based on adsorption.
7. The evaporation of water from a lake can be stopped by depositing monolayer of a suitable substance.
8. The end-point of the precipitation titrations can be detected by using dyes as adsorption indicators.
9. The phenomenon of adsorption is employed for the recovery of vitamins and other biological substances.
10. Chromatography, which is a useful technique for separating and analyzing minute quantities of various components from a mixture, is based on adsorption.

COLLOIDS AND COLLOIDAL SOLUTIONS

What is Colloid?

- *Colloid is a system containing entities having at least one length scale (diameter) in between 1 nm and 1 μm. The word colloid itself originates from a Greek word meaning 'glue-like'.*



Therefore a colloidal is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium.

Simple colloidal dispersions are, therefore, two-phase systems;

- i. dispersed phase (for the phase forming the particles)
- ii. dispersion medium (for the medium in which the particles are distributed).

Examples of systems which are colloidal (at least in some respects) are:

- Aerosols, Agrochemicals, Cement, Cosmetics, Dyestuffs, Emulsions, Fabrics, Foams, Foodstuffs, Ink, Paint, Paper, Pharmaceuticals, Plastics, Rubber, Soil.

Examples of processes which rely heavily on the application of colloid/surface phenomena are:

- Adhesion, Chromatography, Detergency, Ore flotation, Precipitation, Road surfacing, Electrophoretic deposition, Sewage disposal, Emulsion polymerization, Soil conditioning, Food processing, Sugar

refining, Grinding , Water clarification, Heterogeneous catalysis, Water evaporation control, Ion exchange, Water repellency, Lubrication Wetting, Oil-well drilling.

Classification of colloidal systems

Colloidal systems may be grouped into three general classifications:

1. **Colloidal dispersions** are thermodynamically unstable owing to their high surface free energy and are irreversible systems in the sense that they are not easily reconstituted after phase separation.
2. **True solutions of macromolecular material** (natural or synthetic) are thermodynamically stable and reversible in the sense that they are easily reconstituted after separation of solute from solvent.
3. **Association colloids** which are thermodynamically stable.

What is a dispersion?

A dispersion is a collection of small particles in a matrix.

Stable dispersion

A stable dispersion is one in which the dispersed particles remain single entities and do not coagulate. Coagulation leads to phase splitting and a complete change in the properties of the system. For example, during purification of water, coagulation occurs so that all the impurities come together and can be disposed of easily.

Types of stabilities

- i. Thermodynamic stability
- ii. Kinetic stability

Thermodynamically unstable system; when there exists a state where the system will have lower energy than it currently has. A dispersion can be thermodynamically unstable, but can still be kinetically stable.

Kinetically stable dispersion; If in a dispersion (even if it is thermodynamically unstable) the particles do not coagulate for a very long period of time.

Classification of colloids on the basis of;

1. Physical state of dispersed phase and dispersion medium
2. Nature of interaction between dispersed phase and dispersion medium.
3. Types of particles of dispersed phase.

I. Classification based on physical state of dispersed phase and dispersion medium:-

Dispersed phase	Dispersion medium	Types of colloids	Example
Solid	Solid	Solid sol	Some coloured glasses
Solid	Liquid	Sol	Paints
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, jellies
Liquid	Liquid	Emulsion	Milk, Hair cream
Liquid	Gas	Aerosol	Fog, mist
Gas	Solid	Solid sol	Pumice, Stone
Gas	Liquid	Foam	Froth, Whipped cream

II. Classification based on nature of interaction between dispersed phase and dispersion medium

The colloidal system in which a solid is dispersed in a liquid is given the general name 'Sol'. When the dispersion medium is water, the soles are called *hydrosols* or sometimes "*aquasols*". If the dispersion medium is alcohol, the soles are called *alcosols*. When the dispersion medium is benzene, the soles are called *benzosols*. Based on interaction a phases, sols are divided into two categories *lyophilic* sols and *lyophobic* sols.

a) Lyophilic sols (solvent loving)

These are the colloidal solution in which the dispersed phase shows a definite affinity for the dispersion medium or the solvent, when lyophilic sols are precipitated they can easily be converted back into soles by addition of the dispersed medium. Hence are also called reversible sols and behave like true solutions to sonic extent. They are more stable than the lyophobic sols e.g. gums, starches and proteins.

b) Lyophobic sols (solvent hating)

These are the colloidal solution in which the dispersed phase shows very little affinity for the dispersed medium and disperse phase. On heating or cooling the lyophobic systems, solids are obtained which cannot be reconverted into sols either by adding solvent or by warming. Hence are also called irreversible sols. Lyophobic sols are not very stable. Typical examples of this category of colloids are sols of metals, sulphur and silver halides.

Characteristics of Lyophobic and Lyophilic Colloids

Lyophobic Colloids

1. These are generally unstable, get easily coagulated on adding electrolytes.
2. These sols are irreversible in nature.
3. Prepared by indirect methods.
4. Viscosity of colloidal dispersion is same as that of the solvent.
5. These are generally inorganic materials i.e. metals, sulphide and oxide sols.
6. Particles carry positive or negative charge and stability depends on Zeta potential.
7. Surface tension is similar to that of the dispersion medium.
8. The particles present can easily be
9. Examples; Sulphur in water. detected in the ultra microscope.

Lyophilic Colloids

- 1-Lyophilic colloids very stable and are not easily coagulated by electrolytes.
2. These sols are reversible in nature.
3. Usually prepared by simple solution
4. These are highly viscous systems.
5. Mostly organic materials e.g., starch, proteins, gums etc.
6. Particles may have little or no charge at all.
7. Surface tension is lower than that of the dispersion medium.
8. The particles present cannot be easily detected in the ultra microscope.
9. Examples; gum or starch in water.

Stabilisation of hydrophilic and hydrophobic colloids in water.

They can be stabilised via electrostatic and steric stabilisation. Hydrophilic colloids may have a charge on their surface that attracts oppositely charged ions (H^+ or OH^- present in water) to form a tightly bound layer known as the Stern Layer. The Stern layer is surrounded by a diffuse layer which contains an excess of counter-ions (opposite in charge to the Stern layer) and a deficit of co-ions. The Stern layer and diffuse layer are collectively known as a double layer. Coagulation of a hydrophilic colloid is prevented by mutual repulsion of the double layers.

Hydrophobic colloids may be stabilised by the use of a surfactant, e.g. a long chain fatty acid with a polar head and a non-polar tail. When dispersed in water these molecules arrange themselves spherically so that the polar (hydrophilic) heads are interacting with the polar water molecules and the non-polar (hydrophobic) tails are interacting with each other. This arrangement is called a micelle. The hydrophobic colloid can be stabilized by dissolving in the non-polar interior of the micelle.

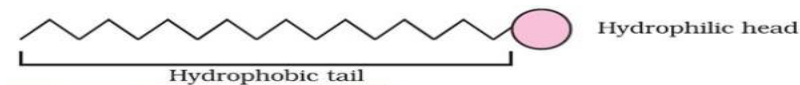


III. **Classification based on type of particle of dispersed phase:-** In it, colloid are classified as multi-molecular, macro-molecular and associated colloids.

- Multimolecular Colloids :-** on dissolution, a large no of substance aggregate together to form species having size in the colloidal range (diameter $<1nm$) the species thus formed are called Multimolecular colloids
- Macromolecular Colloids :-** macromolecules in suitable solvents form solution in which the size of macro molecules may be in colloidal range .such systems are called macromolecule colloids
- Associated Colloids (Micelles):-** these are some substances which at low concentration behave as a normal strong electrolyte, but at higher concentration exhibit colloidal behaviours due to the formation of aggregates, the aggregates particle thus formed are called micelles or associated colloids .the formation of micelles takes place only above a particular temperature called Kraft temperature, and above a particular concentration called *critical concentration* (CMC).

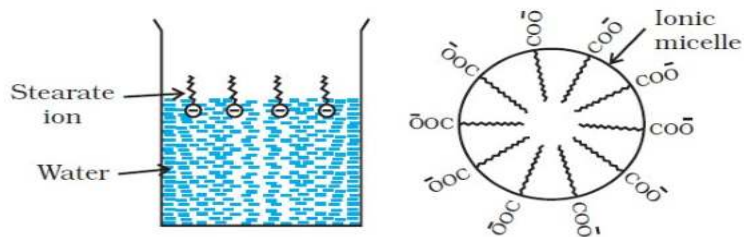
Mechanism of Micelles formation

Soap is the sodium or potassium salt of higher fatty acid and may be represented as $RCOO^- Na$ (e.g. sodium stearate , $(CH_3(CH_2)_{16}COO^-Na^+)$ when dissolve into $RCOO^-$ and Na^+ ions ,the $RCOO^-$ ions ,consist of two parts – a long hydrocarbon chain (also called non – polar tail) which is hydrophobic (water repelling) and a polar group COO^- (polar head) which is hydrophilic (water loving).

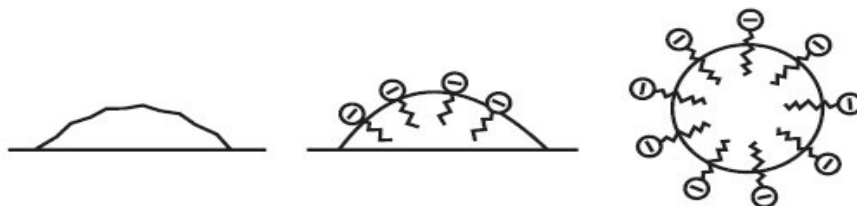


But, at critical micelle concentration the anions are pulled into the bulk of the solution and aggregate to form a spherical shape with their hydrocarbon chain pointing towards the center of the sphere with COO^- part remaining outward on the surface of the sphere .

An aggregate thus formed is known as Ionic micelle



Cleansing action of soaps :- the soap molecule in such a way that hydrophobic part of the stearate ions is in oil droplet and hydrophilic part projects out of the grease droplet like the bristles (hairs)



Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface thus soap help in emulsification and washing away of oils and fats

COLLOIDAL SOLUTION

It is defined as a heterogeneous system consisting of two phases.

- i. A dispersed phase consisting of the colloidal particles.
- ii. A dispersion medium in which the dispersion of the particles takes place and it forms the major portion of the solution.

The particles of the colloidal solutions can pass through an ordinary filter paper but not through an animal membrane. It is obviously impossible to draw a boundary line between true solutions and colloidal solutions.

Examples: Dispersion of oil in water and dispersion of Arsenic sulphide in water forms colloidal solutions.

Preparation of colloidal solutions

Common forms of colloidal solutions to prepare are;

- a. *Aerosols*; dispersions of liquids and solids in air and sometimes in other gases.
- b. *Sols*; dispersions of solids in liquids.
- c. *Emulsion*; dispersions of liquids in liquids.

There are two ways in which colloidal size particles can be obtained

(a). Condensation or aggregation methods- *By building up the particles from single molecules*

(b) Dispersion methods- *By disintegrating down the bulk material to the colloidal particles.*

(1) CONDENSATION METHODS

A supersaturated solution of the disperse phase is prepared in the dispersion medium by carefully controlling the temperature and keeping the concentration of disperse phase to be low. The various methods used here are:

(a) Reduction method

This method is generally used for the preparation of metal sols and involves the reduction of soluble salts of metals by reducing agents, such as formaldehyde, hydrazine or tannic acid. For example: Silver sol can be obtained by reacting dilute AgNO_3 solution with reducing agent like Tannic acid.

$\text{AgNO}_3 + \text{Tannic acid} \longrightarrow \text{Silver sol.}$

b) Oxidation method

This method is used for the preparation of colloidal sulphur by the oxidation of hydrogen sulphide. This oxidation may be done by passing hydrogen sulphide through a solution of sulphur dioxide in water.



c) Hydrolysis method

this method is used to obtain sols of oxides or hydroxides of weakly electropositive metals like iron, aluminium etc. for example a Ferric hydroxide sol obtained by adding a small quantity of ferric chloride into a large excess of boiling water.



d) Double decomposition method

Arsenic sulphide sol is obtained by mixing solution of arsenious oxide and hydrogen sulphide when double displacement takes place.



The excess hydrogen sulphide is removed by passing a stream of hydrogen.

e) Exchange of solvent method

This method is based on the principle that if a substance 'A' is insoluble in one solvent say 'X' in another Y then the colloidal solution of substance 'A' is prepared by dissolving it in solvent 'Y' and pouring the solution into an excess of solvent 'X'. this method is used to prepare sulphur or phosphorus sols by first dissolving them in alcohol and pouring their alcoholic solution into water

2) DISPERSION METHODS

These methods involve the breaking of bigger particles into particles of colloidal size. Various methods used for this purpose are:

(i) Mechanical dispersion method

In this method the substance is finely ground and then shaken with a dispersion medium to get a coarse suspension. This suspension is then changed to particles of colloidal size by means of colloidal mill. This mill consists of two metal discs nearly touching each other and rotating in opposite direction at very high speed (7,000 revolutions per minute). The suspension passes through the rotating discs and is broken down to particles of colloidal size. Examples; colloidal graphite (a lubricant) and printing inks are made by this method.

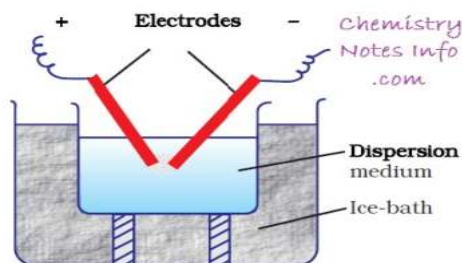
(ii) Peptisation method

The process of dispersing a precipitated material into a colloidal solution by adding a small quantity of an electrolyte is called peptisation. The electrolyte added is called a peptisation agent. and mostly contains a common ion.

Example; freshly prepared precipitates of ferric hydroxide when treated with a small amount of FeCl_3 solution (peptizing agent) results in the formation of a dark reddish brown sol.

(iii) Electro-dispersion or Bredig's method

This method involves both dispersion and condensation processes. In this method, an electric arc is produced inside water (solvent) between the two electrodes of the metal to be dispersed. The heat of the arc evaporates the metal. These vapours of the metal are condensed by the ice cold water to form a colloidal solution. A small amount of KOH is added in the dispersion medium to stabilize the sol. This method is used for preparing the hydrosols of metals. Such as Ag, Au, Cu and Pt.

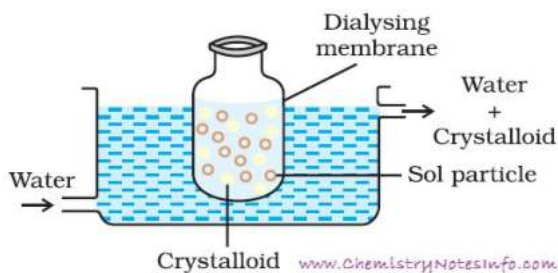


PURIFICATION OF COLLOIDAL SOLUTION -PURIFICATION OF SOL

A sol prepared by any one of the above methods very often contains other material besides the colloidal particles. It is necessary to remove these impurities as they reduce the stability of the sols. The purification of sols can be done by means of the following FOUR methods;

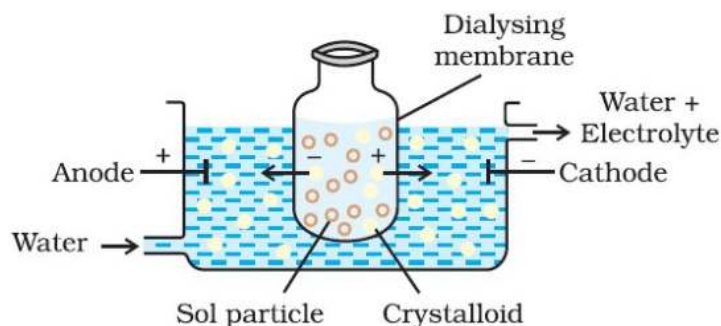
- i. Dialysis
- ii. Electro dialysis
- iii. Ultra filtration
- iv. Ultra centrifugation

(I) Dialysis

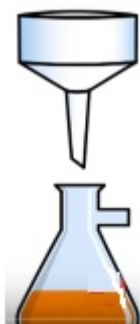


It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane. Since, particles (ions or smaller molecular) in a true solution can pass through an animal membrane (bladder) or parchment paper or colloidal particles, the molecules and ions diffuse through membrane into the outer water and pure colloidal solution is left behind.

(II) Electro dialysis: - The process of dialysis is quite slow it can be made faster by applying an electric field electrodes are fitted in the compartment. The ions present in the colloidal solution migrate out to the oppositely charge to electrodes.



(III) Ultra filtration: - In these methods special filters are used, which are permeable to all substances except the colloidal particles. An ultra filter paper may be prepared by soaking the filter paper in a colloidal solution, hardening by formaldehyde and then finally drying it. Thus, by using ultra filter paper the colloidal particles are separated from rest of the materials. The colloidal particles left on the ultra filter paper are there stirred with fresh dispersion medium (solvent) to get a pure colloidal solution.



(IV) Ultra centrifugation; this technique employs a very high speed centrifugal machine, capable of generating acceleration as high as 19600 km/s^2 (around 50000 rpm). The colloidal particles are segregated from the impure medium and then suitably peptized in pure medium.

Properties of Colloidal Solutions :

(1) *Physical properties :*

(i) ***Heterogeneity :*** Colloidal solutions are heterogeneous in nature consisting of two phases viz, the dispersed phase and the dispersion medium. Experiments like dialysis and ultra filtration clearly indicate the heterogeneous character of colloidal system. Recent investigations however, shown that colloidal solutions are neither obviously homogeneous nor obviously heterogeneous.

(ii) ***Filterability :*** Colloidal particles readily pass through ordinary filter papers. It is because the size of the pores of the filter paper is larger than that of the colloidal particles.

(iii) ***Non-settling nature :*** Colloidal solutions are quite stable as the colloidal particles remain suspended in the dispersion medium indefinitely. Thus there is no effect of gravity on the colloidal particles.

(iv) ***Colour :*** The colour of the colloidal solution is not always the same as the colour of the substances in the bulk. The colour of the colloidal solution depends upon the following factors:

(a) Size and shape of colloidal particles.

- (b) Wavelength of the source of light.
- (c) Method of preparation of the colloidal solution.
- (d) Nature of the colloidal solution.
- (e) The way an observer receives the light, i.e., whether by reflection or by transmission.

Stability : Colloidal solutions are quite stable. Only a few solutions of larger particles may settle but very slowly.

Examples :

- (i) Finest gold is red in colour. As the size of particles increases, it becomes purple.
- (ii) Dilute milk gives a bluish tinge in reflected light whereas reddish tinge in transmitted light.

(c) Diffusibility; The colloidal particles have a very little ability to diffuse because of their large size as compared to the solute particles present in the solution.

(e) Surface tension and viscosity; The surface tension and viscosity of sols depend on their nature. For lyophobic sol, the surface tension and viscosity are not very much different from that of the medium because of very little interaction between colloidal particles and the molecules of the medium. On the other hand lyophilic sols show variation in these properties because of the presence of interactions. Thus the viscosity of the lyophilic sols is much higher than the medium but the surface tension is generally lower than that of the pure medium.

(2) Mechanical Properties :

(a) Brownian movement : Colloids particles exhibit a ceaseless random and swarming motion. This kinetic activity of particles suspended in the liquid is called Brownina movement.

Robert Brown first observed this motion with pollen grains suspended in water.

Cause of movement : Brownian movement is due to bombardment of the dispersed particles by molecules of the medium. The Brownian movement (figure) depends upon the size of sol. particles. With the increase in the size of the particle, the chance of unequal bombardment decrease, and the Brownial movement too disappears. It is due to the fact that the suspension fails to exhibit this phenomenon.

It should be noted that Brownian movement does not change with time but changes with temperatures.



Importance :

- i. Brownian movement is a direct demonstration of the assumption that the molecules in a gas or solution are in a state of constant ceaseless motion. Thus it confirms kinetic theory.
- ii. Brownian movement does not allow the colloidal particles to settle down due to gravity and thus is responsible for their stability.
- iii. Brownian movement helps to calculate the Avogadro's number.

(b) **Sedimentation** : Heavier sol. particle tend to settle down very slowly under the influence of gravity. This phenomenon is called sedimentation.

(3) **Optical Properties (Tyndal Effect) :**

When a strong and converging beam of light is passed through a colloidal solution, its path becomes visible (bluish light) when viewed at right angles to the beam of light (figure). This effect is called Tyndall effect. The light is observed as a bluish cone which is called Tyndall cone.

The Tyndall effect is due to scattering of light by the colloidal particles. The scattering of light cannot be due to simple reflection, because the size of the particles is smaller than the wave, length of the visible light and they are unable to reflect light waves. In fact, colloidal particles first absorb light and then a part of the absorbed light is scattered from the surface of the colloidal particles as a light of shorter wavelength. Since maximum scattering of light takes place at right angles to the place of incident light, it becomes visible when seen from that direction.

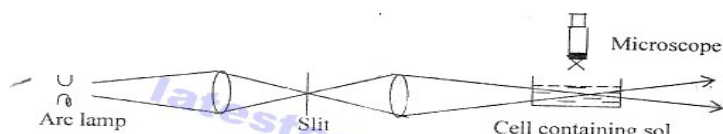


Fig.3.7. Arrangement of ultra microscope.

The Tyndall effect is observed under the following conditions :

- (i) The diameter of the dispersed particles must not be much smaller than the wavelength of light employed.
- (ii) The refractive indices of the dispersed phase and the dispersion medium must differ widely. This condition is fulfilled by lyophobic colloids.

It is important to note that Tyndall effect is not shown by true solutions as their particles are too small to cause scattering. Tyndall effect has been used in devising ultra microscope and in determining the number of colloidal particles in a colloidal solution.

Determination of molecular weight by light scattering

In liquid dispersions, the scattering of light is due to fluctuations in the solvent density and fluctuations in the particle concentration. The total intensity of the scattered light in all directions is given by;

$$I_s = I_0 \int_0^\pi \left(\frac{i_s}{I_0} \right) (2\pi r^2 \sin \phi d\phi) \tag{1}$$

The second term inside the integral in Eq. (1) represents an area on the surface of a sphere, where r is the radius of the sphere and ϕ is the angle with the horizontal axis. From the theory of Rayleigh scattering in a solution, the quantity i_s/I_0 can be determined as shown below. The Rayleigh scattering equation for a solution (at constant temperature) is expressed by,

$$\frac{i_s}{I_0} = \frac{2\pi^2 \left[n_r \left(\frac{dn_r}{dc} \right) \right]^2 kTc}{r^2 \lambda^4 \left(\frac{d\pi_o}{dc} \right)} (1 + \cos^2 \phi) \quad (2)$$

where i_s is the intensity of the light scattered per unit volume of solution. The gradient of refractive index of the solution n_r , is given by dn_r/dc .

The osmotic pressure is given by,

$$\pi_o = RT \left(\frac{c}{M} + \frac{B'}{RT} c^2 \right) = RT \left(\frac{c}{M} + Bc^2 \right), \quad B = \frac{B'}{RT} \quad (3)$$

Where

- M is the molecular weight of the solute,
- c is the concentration,
- B is the second virial coefficient.

Therefore, the osmotic pressure gradient is given by;

$$\frac{d\pi_o}{dc} = RT \left(\frac{1}{M} + 2Bc \right) \quad (4)$$

From Eq. (2), we can write,

$$\frac{i_s}{I_0} = \frac{Kc(1 + \cos^2 \phi)}{r^2 (1/M + 2Bc)} \quad (5)$$

The quantity K is a constant, which is given by;

$$K = \frac{2\pi^2 \left[n_r \left(\frac{dn_r}{dc} \right) \right]^2}{N_A \lambda^4} \quad (6)$$

From Eqs. (1) and (6) we obtain;

$$\frac{I_s}{I_0} = \int_0^\pi \left[\frac{2\pi Kc(1 + \cos^2 \phi) \sin \phi d\phi}{1/M + 2Bc} \right] \quad (7)$$

The value of the integral:

$$\int_0^\pi \sin \phi (1 + \cos^2 \phi) d\phi \text{ is } 8/3$$

. Therefore, Eq. (7) becomes,

$$\frac{I_s}{I_0} = \frac{16\pi Kc}{3(1/M + 2Bc)} = \frac{Hc}{1/M + 2Bc} \quad (8)$$

Where

$H(\equiv 16\pi HK/3)$ is a constant. It is related to the refractive index, its gradient and the wavelength of light in the medium by the following equation.

$$H = \frac{32\pi^3 n_r^2 (dn_r/dc)^2}{3N_A \lambda^4} \quad (9)$$

where

- λ is the wavelength of light in the solution
- N_A is Avogadro's number. The quantity I_s/I_0 is the turbidity, τ .

Therefore, from Eq. (8) we have,

$$\frac{Hc}{\tau} = \frac{1}{M} + 2Bc \quad (10)$$

Equation (10) is known as *Debye equation*. It predicts that the plot of Hc/τ versus c should be a straight line. From the intercept, the molecular weight M can be determined.

Example 1.4.1: The variation of Hc/τ with concentration for a polymeric colloid in benzene is given below.

c (kg/m ³)	2.5	4.0	6.5	8.0	10.0
$(Hc/\tau) \times 10^3$ (mol/kg)	5.6	6.1	6.6	7.2	8.0

From these data, calculate the molecular weight of the polymer.

Solution: The plot of Hc/τ vs. c is shown in the following figure. The data were fitted by a straight line, as shown in Fig. 1.4.1.

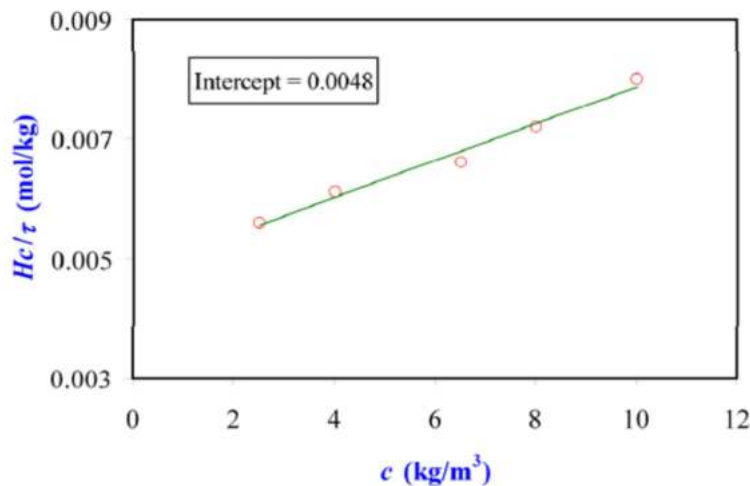


Fig. 1.4.1 Variation of Hc/τ with concentration.

Fig. 1.4.1 Variation of Hc/τ with concentration.

The intercept is,

$$\frac{1}{M} = 0.0048 \text{ mol/kg}$$

$$\therefore M = 208.333 \text{ kg/mol}$$

If the system is poly dispersed, Eq. (10) is applicable for each molecular weight fraction. For dilute solutions, we can neglect the second term on the right side of Eq. (10). For the j^{th} fraction, we can write,

$$\frac{Hc_j}{\tau_j} = \frac{1}{M_j} \quad (11)$$

The experimentally measured concentration, turbidity and the average molecular weight are correlated by Equation (11) as,

$$\frac{Hc_{\text{exp}}}{\tau_{\text{exp}}} = \frac{1}{\bar{M}} \quad (12)$$

where,

$$c_{\text{exp}} = \sum c_j \quad (13)$$

and

$$\tau_{\text{exp}} = \sum \tau_j \quad (14)$$

From Eqs. (11)–(14), we obtain,

$$\bar{M} = \frac{\tau_{\text{exp}}}{Hc_{\text{exp}}} = \frac{\sum \tau_j}{H \sum c_j} = \frac{H \sum c_j M_j}{H \sum c_j} = \frac{\sum c_j M_j}{\sum c_j} \quad (15)$$

Since $c_j = n_j M_j / V_d$, we have,

$$\bar{M} = \frac{\sum n_j M_j^2}{\sum n_j M_j} \quad (16)$$

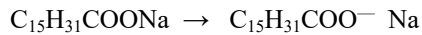
This average molecular weight (i.e., \bar{M}) is known as the *weight-average molecular weight*.

(4) **Electrical Properties :**

Origin of charge: Various reasons have been given regarding the original of charge on the colloidal particles. These are given below:

(i) **Frictional electrification :** It is believed to be frictional due to the rubbing of the dispersed phase particles with medium molecules.

(ii) **Dissociation of the surface molecules :** It leads to electric charge on colloidal particles. For example, an aqueous solution of a soap (sodium palmitate) dissociates into ions.



sod. palmitate

The Na⁺ ions pass into the solution while C₁₅H₃₁COO⁻ ions have a tendency to form aggregates due to weak attractive forces present in the hydrocarbon chains. Thus, the anions which are of colloidal size bear negative charge.

(iii) **Preferential adsorption of ions from solution** : The charge on the colloidal particles is generally acquired by preferentially adsorbing positive or negative ions from the electrolyte. Thus AgCl particles can adsorb Cl⁻ ions from chloride solutions and Ag⁺ ions from excess Ag ions solutions; the sol. will be negatively charged in the first case and positively charged in the second case.

(iv) **Capture of electron**: It is from air during preparation of sol. by Bredig's arc method.

(v) **Dissociation of molecular electrolytes on the surface of particles** : H₂S molecules get adsorbed on sulphides during precipitation. By dissociation of H₂S, H⁺ ions are lost and colloidal particles become negatively charged.

Electrical charged sols.

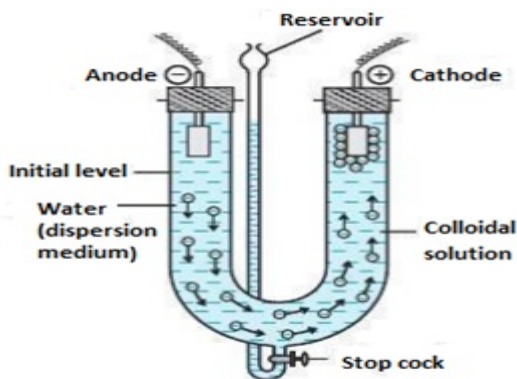
Positively charged sols	Negatively charged sols
1. Ferric hydroxide, aluminium hydroxide	1. Metals such as Pt, Au, Ag, Metals sulphides, e.g. arsenious sulphide.
2. Basic dyes such as methylene blue	2. Starch, clay, silicic acid.
3. Haemoglobin	3. Acid dyes, such as eosin

The two electrical properties of colloidal solutions are :

- i. **Electrophoresis or Cataphoresis**
- ii. **Electro-osmosis**

(a) **Electrophoresis or Cataphoresis** :

In a colloidal solution, the colloidal particles are electrically charged and the dispersion medium has equal but opposite charge. Thus colloidal solution on the whole is electrically neutral. When an electric current is passed through a colloidal solution, the charged particles move towards the oppositely charged electrode where coagulate due to loss of charge.



The phenomenon involving the migration of colloidal particles under the influence of electric field towards the oppositely charged electrode, is called *electrophoresis or cataphoresis*.

This phenomenon is used to determine the charge on the colloidal particles. For example, when a sol. of ferric hydroxide is taken in a U-tube and subjected to electric field, the ferric hydroxide (sol.) particles get accumulated near the cathode (figure). This shows that ferric hydroxide sol. particles are positively charged.

The sol. particles of metals and their sulphides are found to be negatively charged while those of metal hydroxides are positively charged. Basic dyes such as methylene blue haemoglobin are positively charged while acid dyes like are negatively charged.

(b) **Electro-osmosis :**

The phenomenon involving the migration of the dispersion medium and not the colloidal particles under the influence of an electric field is electro-osmosis.

Take the pure solvent (dispersion medium) in two limbs of U-tube. In the lower middle portion of U-tube, a porous diaphragm containing the colloidal system is present which divides the U-tube in two sections. In each section of U-tube, an electrode is present, as shown in figure. When the electrode potential is applied to the electrodes, the solid phase of sol. (colloidal system) cannot move but the solvent (dispersion medium) moves through the porous diaphragm towards one of the electrodes. The direction of migration of dispersion medium due to electro-osmosis determines the charge on sol. particles e.g., if the dispersion medium moves towards the cathode (negative electrode), the sol. particles are also negatively charged because the dispersion medium is positively charged as on the whole colloidal solution is neutral.

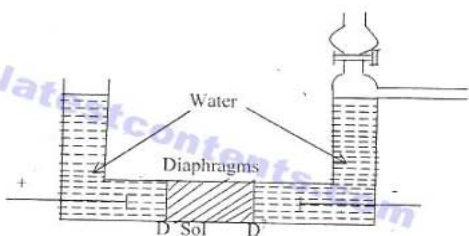


Fig.3.10. Apparatus used for electro-osmosis.

Electrical double layer and zeta potential

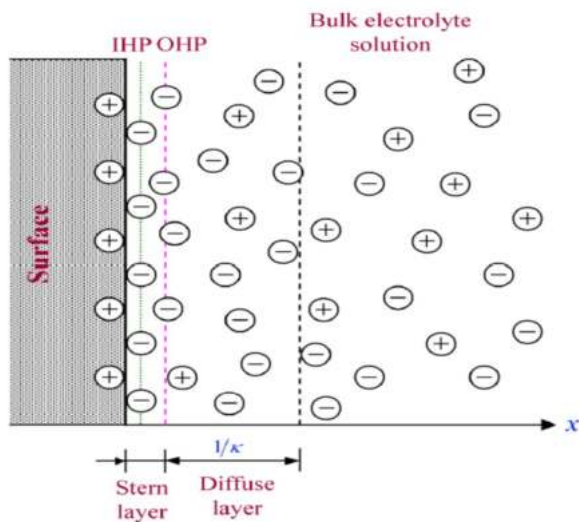
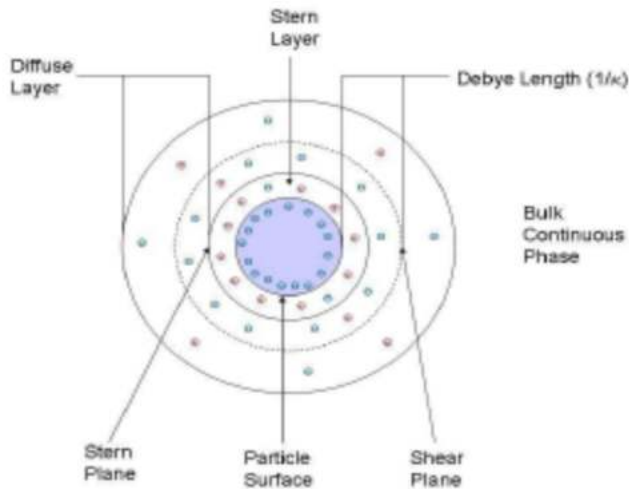
(i) Double layer

It is the combination of two layers of positive and negative charges around the sol particles. The double layer is made up of;

- The inner (Stern) layer -consists of ions that are electrostatically attracted to the charged particle.
- The outer (diffuse) layer -consists of counter ions (containing opposite ions).

These layers were observed by Helmholtz, hence it is also called *Helmholtz double layer*. According to Helmholtz, the charges next to the particle surface were fixed while the compensating charges along the medium were mobile.

The combination of the compact and diffused layer is called the *stern double layer*.



Sources of interfacial charge

An interface may acquire an electrical charge by one or more of several mechanisms, the most common of which include;

- (1) preferential (or differential) solution of surface ions,
- (2) direct ionization of surface groups,
- (3) substitution of surface ions,
- (4) specific ion adsorption
- (5) charges deriving from specific crystal structures

The Debye Length and Double-Layer Thickness:

a) Debye length

The Debye length, κ^{-1} , can be calculated from the following Debye–Huckel approximation equation.

$$\kappa^{-1} = \left[\frac{N_A e^2}{\epsilon \epsilon_0 k T} \sum_i z_i^2 c_i^\infty \right]^{-1/2} \quad \text{OR} \quad \frac{1}{\kappa} = \left(\frac{\epsilon_0 \epsilon k T}{e_i^2 \sum c_i z_i^2} \right)^{1/2}$$

where

- c_i^∞ is the concentration of ions of type i, expressed in mol/m³
- Z is the Charge on the ion.
- k (has a unit of m⁻¹) is identified as the reciprocal of the thickness of the electrical double layer, also commonly referred to as the “Debye length.” Thus at a distance of 1/k from a charged surface, the potential has fallen off by a factor of 1/e.

In aqueous medium at 298 K, $\frac{N_A e^2}{\epsilon \epsilon_0 k T} = 5.404 \times 10^{15} \text{m}^{-1}$

Therefore, the above Eq. can be written as,

$$\kappa^{-1} = \left[5.404 \times 10^{15} \sum_i z_i^2 c_i^\infty \right]^{-1/2}$$

Where;

- c_i is the concentration of ions of type i, expressed in mol/l
- Z is the Charge on the ion.

OR

$$\kappa^{-1} = \frac{1}{2.32 \times 10^9 [\sum Z_i^2 C_i]^{1/2}}$$

$$\text{i.e } \kappa = 2.32 \times 10^9 [\sum Z_i^2 C_i]^{-1/2}$$

When c - the concentration of ions is expressed in mol/l or mol/dm³

Example :

Calculate the Debye lengths in 10 mol/m³ aqueous solutions of NaCl, CaCl₂ and AlCl₃ at 298 K.

Solution: Let us calculate the Debye lengths using Eq. (3.3.18).

$$\text{For NaCl: } \sum_i z_i^2 c_i^\infty = (1)^2 \times 10 + (1)^2 \times 10 = 20 \text{ mol/m}^3$$

$$\kappa^{-1} = \left[5.404 \times 10^{15} \times 20 \right]^{-1/2} = 3.04 \times 10^{-9} \text{ m}$$

$$\text{For CaCl}_2: \sum_i z_i^2 c_i^\infty = (2)^2 \times 10 + (1)^2 \times 2 \times 10 = 60 \text{ mol/m}^3$$

$$\kappa^{-1} = \left[5.404 \times 10^{15} \times 60 \right]^{-1/2} = 1.76 \times 10^{-9} \text{ m}$$

$$\text{For AlCl}_3: \sum_i z_i^2 c_i^\infty = (3)^2 \times 10 + (1)^2 \times 3 \times 10 = 120 \text{ mol/m}^3$$

$$\kappa^{-1} = \left[5.404 \times 10^{15} \times 120 \right]^{-1/2} = 1.24 \times 10^{-9} \text{ m}$$

b) Double layer

For the thickness of the diffuse **double layer**, the Eq. becomes,

$$\kappa^{-1} = \left[2 \times 5.404 \times 10^{15} \sum_i Z_i^2 C_i \right]^{-1/2} = \left[10.808 \times 10^{15} \sum_i Z_i^2 C_i \right]^{-1/2} = 9.6 \times 10^{-9} \left[\sum_i Z_i^2 C_i \right]^{-1/2} \text{ (where } c = \text{mol/m}^3 \text{)}$$

Or

$$\kappa^{-1} = \frac{1}{3.29 \times 10^9 \left[\sum_i Z_i^2 C_i \right]^{1/2}}$$

$$\text{i.e. } \kappa = 3.29 \times 10^9 \left[\sum_i Z_i^2 C_i \right]^{1/2}$$

Where;

- c_i is the concentration of ions of type i , expressed in mol/l
- Z is the Charge on the ion.

Example

Calculate the thickness of the diffuse double layer for a negatively charged solid in contact with aqueous solutions of the following concentrations at 25°C. [8 marks]

- 0.010 M KCl;
- 0.0010 M KCl;
- 0.0010 M K₂SO₄;
- 0.0010 M MgCl₂.

a)

$$\kappa = 3.29 \times 10^9 (cZ^2)^{1/2} \text{ m}^{-1}$$

$$\frac{1}{\kappa} = \text{Debye Length} = \frac{1}{3.29 \times 10^9 (0.010 \text{ M} \times 1^2)^{1/2}} \text{ m} = 3.0 \times 10^{-9} \text{ m}$$

b)

$$\frac{1}{\kappa} = \frac{1}{3.29 \times 10^9 (0.0010 \text{ M} \times 1^2)^{1/2}} \text{ m} = 9.6 \times 10^{-9} \text{ m}$$

c)

$$\frac{1}{\kappa} = \frac{1}{3.29 \times 10^9 (0.0020 \text{ M} \times 1^2)^{1/2}} \text{ m} = 6.8 \times 10^{-9} \text{ m}$$

d)

$$\frac{1}{\kappa} = \frac{1}{3.29 \times 10^9 (0.0010 \text{ M} \times 2^2)^{1/2}} \text{ m} = 4.8 \times 10^{-9} \text{ m}$$

Summary

For ease of calculation of $1/k$, Equation above can be simplified to the following relationships:

For 1:1 electrolytes:

$$1/k = 0.304 [\text{MX}]^{1/2}$$

For 2:1 and 1:2 electrolytes:

$$1/k = 0.178 [\text{MX}_2]^{1/2} \text{ (or } [\text{M}_2\text{X}]^{1/2})$$

For 2:2, 3:1, or 1:3 electrolytes:

$$1/k = 0.152 [\text{M}_2\text{X}_2]^{1/2} \text{ (or } [\text{MX}_3]^{1/2} \text{ or } [\text{M}_3\text{X}]^{1/2})$$

For 2:3 or 3:2 electrolytes:

$$1/k = 0.136 [\text{M}_3\text{X}_2]^{1/2} \text{ (or } [\text{M}_2\text{X}_3]^{1/2})$$

Double-Layer Thickness ($1/k$) for Various Electrolytes in Water ($1/k$)(nm) Electrolyte

Concentration	1:1 (MX)	1:2 (MX ₂)	2:2 (MX)	1:3 (MX ₃)	2:3 (M ₂ X ₃)
10 ⁴	30.4	17.6	15.2	15.2	13.6
10 ³	9.6	5.57	4.81	4.81	4.30
10 ²	3.0	1.76	1.52	1.52	1.36
10 ¹	0.96	0.56	0.48	0.48	0.43
1	0.30	0.18	0.15	0.15	0.14

Calculate the Debye length $1/K$ for the following solutions:

(a) pure water ($K_w = 10^{-14}$);

(b) 0.1 M NaCl;

(c) 0.01 M NaCl;

- (d) 1mM NaCl;
 (e) 0.1 M CaSO₄;
 (f) 1.0 mM La(NO₃)₃.

(ii) Zeta (ζ) potential

The zeta potential is a measure of repulsion between adjacent, similarly charged particles in a colloid (i.e. the stability of a colloid). The magnitude of ζ -potential provides an indication of the stability of the colloid system. Colloids with high zeta potentials are electrically stabilized, whilst those with low potentials tend to coagulate. Because of the distribution of the charge around the particle, there is a difference in potential between the compact layer and the bulk of the solution across the diffused layer. This is called Electro kinetic or *Zeta potential*.

Zeta potential can be calculated with the following Smoluchowski's formula:

$$\zeta = \frac{4\pi\eta}{\epsilon} \times U \times 300 \times 300 \times 1000$$

ζ = Zeta Potential (mV) η = Viscosity of Solution ϵ = Dielectric Constant $U = \frac{v}{V/L}$: Electrophoretic Mobility v = Speed of Particle (cm/sec) V = Voltage (V) L = The distance of Electrode

The principle of determining zeta potential is very simple. A controlled electric field is applied via electrodes immersed in a sample suspension and this causes the charged particles to move towards the electrode of opposite polarity. Viscous forces acting upon the moving particle tend to oppose this motion and an equilibrium is rapidly established between the effects of the electrostatic attraction and the viscosity drag. The particle therefore reach a constant terminal velocity.

Factors Affecting Zeta Potential

(1) pH

In aqueous media, the pH of the sample is one of the most important factors that affects its zeta potential. Imagine a particle in suspension with a negative zeta potential. If more alkali is added to this suspension then the particles tend to acquire more negative charge. If acid is added to this suspension then a point will be reached where the charge will be neutralised. Further addition of acid will cause a build up of positive charge. Therefore a zeta potential versus pH curve will be positive at low pH and lower or negative at high pH. There may be a point where the plot passes through zero zeta potential. This point is called the *isoelectric point* and is very important from a practical consideration. It is normally the point where the colloidal system is least stable. A typical plot of zeta potential versus pH is shown in figure 8. In this example, the isoelectric point of the sample is at approximately pH 5.5. In addition, the plot can be used to predict that the sample should be stable at pH values

less than 4 (sufficient positive charge is present) and greater than pH 7.5 (sufficient negative charge is present). Problems with dispersion stability would be expected at pH values between 4 and 7.5 as the zeta potential values are between +30 and -30mV.

2. Conductivity

The thickness of the double layer (κ^{-1}) depends upon the concentration of ions in solution and can be calculated from the ionic strength of the medium. The higher the ionic strength, the more compressed the double layer becomes. The valency of the ions will also influence double layer thickness. A trivalent ion such as Al^{3+} will compress the double layer to a greater extent in comparison with a monovalent ion such as Na^+ .

Inorganic ions can interact with charged surfaces in one of two distinct ways;

- (i) non-specific ion adsorption where they have no effect on the isoelectric point.
- (ii) specific ion adsorption, which will lead to a change in the value of the isoelectric point. The specific adsorption of ions onto a particle surface, even at low concentrations, can have a dramatic effect on the zeta potential of the particle dispersion. In some cases, specific ion adsorption can lead to charge reversal of the surface.

3. Concentration of a formulation component

The effect of the concentration of a formulation component on the zeta potential can give information to assist in formulating a product to give maximum stability. The influence of known contaminants on the zeta potential of a sample can be a powerful tool in formulating the product to resist flocculation for example.

Measurement of the zeta potential

The zeta potential can be determined with four different measurement techniques called *Electrokinetic phenomena*. *Electrokinetic phenomena*- it is the phenomena associated with the movement of charged particles through a continuous medium, or with the movement of a continuous medium over a charged surface. There are four major types of electro kinetic phenomena;

- i. *Electrophoresis*; The movement of a charged interface (usually colloidal particles or macromolecules) plus its electrical double layer relative to a stationary liquid, under the influence of an applied field. Electrophoresis is, of course, the complement of electroosmosis.
- ii. *Electroosmosis*; The movement of a liquid relative to a stationary charged interface under the influence of an electric field. The fixed surface will typically be a capillary tube or porous plug.
- iii. *Streaming Potential*; The electric field generated when a liquid is forced to flow past a stationary charged interface.
- iv. *Sedimentation Potential*; The electric field produced when charged particles move relative to a stationary liquid.

There is a common origin for all the electro kinetic phenomena, i.e., the electrostatic double layer.

a) Electrophoresis

Electrophoresis refers to the movement of particles relative to a stationary liquid under the influence of an applied electric field. If a dispersion of positively charged particles is subjected to an electric field, the particles move towards the cathode. Three types of electrophoresis are usually used;

- i. micro electrophoresis,
- ii. Moving-boundary electrophoresis.
- iii. Zone electrophoresis.

The velocity of the colloidal particles under a fall of potential one volt per cm. is known as the *electrophoretic mobility*. On applying the voltage the boundary between the sol (positively charged ferric hydroxide sol) and water begins to move towards the cathode. The level of water falls gradually on the side of the positive electrode and rises on the side of the negative electrode. On the other hand, if the sol particles are negatively charged, the level gradually falls on the side of the negative electrode and rises on the side of the positive electrode. Thus by noting the direction of movement of sol particles the nature of their charged can be known.

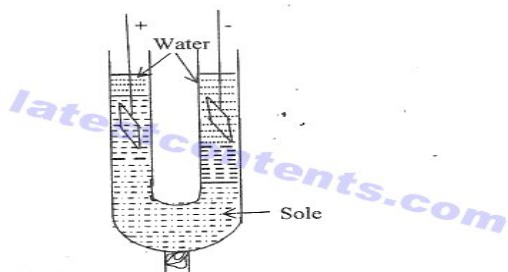


Fig.3.9. Electrophoretic apparatus

Electrophoresis is widely used in biochemical analysis for separation of proteins.

Another very important application of electrophoresis is electrode position.

b) Electro osmosis

The movement of the dispersion medium through a porous material under the influence of an applied electric field is called Electro-osmosis. The sol particles are kept stationary by some suitable means. Electro-osmosis is the inverse of electrophoresis. In electrophoresis, the sol particles move and the dispersion medium remains stationary.

Whereas in electro-osmosis the dispersion medium moves and the sol particles remain stationary. The apparatus used for demonstrating the phenomenon of electro-osmosis is shown in the figure 3.10.

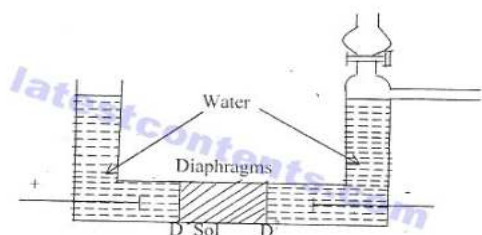


Fig.3.10. Apparatus used for electro-osmosis.

The two diaphragms (D) and (D') divide the apparatus into three compartments. The central compartment is filled with sol while the two-side compartments are filled with water (solvent). The electrode is also fitted in the side

compartments. The diaphragms are made of porous clay. When an electric field is applied across the two electrodes, water (dispersion medium) is observed to move. The direction of flow of water depends on the charge of the particles present in the sol. The applications of electro-osmosis are as follow;

- i. Electro-osmosis is used to remove water from peat.
- ii. The process is used for the removal of water in moist clay.

c) Streaming current and streaming potential

Streaming potential - the electric field which is created when liquid is made to flow along a stationary charged surface (i.e. the opposite of electro-osmosis). The liquid in the capillary or plug carries a net charge (that of the mobile part of the electric double layer) and its flow gives rise to a *streaming current* and, consequently, a potential difference. This potential opposes the mechanical transfer of charge by causing back conduction by ion diffusion and, to a much lesser extent, by electro-osmosis. The transfer of charge due to these two effects is called the leak current, and the measured streaming potential relates to an equilibrium condition when streaming current and leak current cancel each other.

d) Sedimentation potential

- the electric field which is created when charged particles move relative to stationary liquid (i.e. the opposite of electrophoresis).

If a dispersion of charged particles is allowed to settle, the resulting motion of the particles causes the development of a potential difference between the upper and lower parts of the dispersion. It is known as *Dorn effect* and the potential is known as *sedimentation potential*.

- Therefore, the situations which give rise to streaming potential and sedimentation potential are opposite to those of electro osmosis and electrophoresis, respectively.

Determination of ζ -potential from electrophoresis

- Let us consider the motion of a small spherical colloid particle moving with velocity *u* in an electric field *E*. In a dilute dispersion, the mobility is given by the Hückel equation;

$$\frac{u}{E} = \frac{2\epsilon\epsilon_0\zeta}{3\mu}, \quad \kappa R_s < 0.1 \tag{1}$$

where

- *k* is the Debye-Hückel parameter,
 - ϵ is the dielectric constant of the medium,
 - ϵ_0 is permittivity of the free space,
 - μ is the viscosity of the liquid
 - *Rs* is the radius of the sphere.
- For large values of *kRs* , the relationship between the electrophoretic mobility and ζ -potential is given by Smoluchowski equation (also known as *Helmholtz-Smoluchowski equation*);

$$\frac{u}{E} = \frac{\epsilon\epsilon_0\zeta}{\mu}, \quad \kappa R_s > 100 \tag{2}$$

Equation (18) is applicable for relatively high salt concentrations for which k is large.

- Apart from these two limiting conditions, the zeta potentials for the other values of kRs can be calculated by the following equation.

$$\frac{u}{E} = \frac{2\varepsilon\varepsilon_0\zeta}{3\mu} f(\kappa R_s) \quad (3)$$

where $f(kRs)$ can be calculated from either Henry's or Ohshima's equation. The latter equation is more convenient for computation.

$$f(\kappa R_s) = 1 + \frac{1}{2 \left[1 + \frac{2.5}{\kappa R_s \{1 + 2 \exp(-\kappa R_s)\}} \right]^3} \quad (4)$$

This equation is valid for any value of kRs with maximum relative error less than 1%.

Determination of ζ -potential from electro osmosis

- When an electric field is applied across a capillary containing electrolyte solution, the double layer ions begin to migrate. After some time, a steady state is reached when the electrical and viscous forces balance each other, i.e., the force exerted on the medium by the ions is balanced by the force exerted by the medium on the ions.
- If the steady state volumetric flow rate in a fine capillary due to electro osmosis is V , then the ζ -potential is given by,

$$\zeta = \frac{V\mu}{\varepsilon\varepsilon_0EA}, \quad \kappa R_s \gg 1 \quad (5)$$

where

- Rc is the radius
- A is the cross-sectional area of the capillary.

Therefore, by measuring the volumetric flow rate through the capillary, the ζ -potential can be determined.

Example 2: An aqueous solution of sodium chloride is placed inside a capillary in an electro osmosis apparatus and subjected to an electric field of 100 V/m. The electro osmotic velocity in the capillary is observed to be 10 μ m/s. Calculate ζ -potential from these data.

Solution: The electro osmotic velocity is given by;

$$\frac{V}{A} = 10 \times 10^{-6} \text{ m/s}$$

For water, $\varepsilon = 78.5$, $\mu = 1 \times 10^{-3}$ Pa s, and the permittivity of free space is,

$\varepsilon_0 = 8.854 \times 10^{-12}$ C² J⁻¹ m⁻¹. From Eq. (1.4.21) we obtain,

$$\zeta = \frac{V\mu}{\varepsilon\varepsilon_0EA} = \frac{10 \times 10^{-6} \times 1 \times 10^{-3}}{78.5 \times 8.854 \times 10^{-12} \times 100} = 0.1439 \text{ V} = 143.9 \text{ mV}$$

Determination of ζ potential from streaming potential

- The ζ -potential can be correlated with streaming potential as follows. A pressure difference across a capillary is applied which sets the liquid in motion inside it. The charge of the double layer moves with the surrounding liquid generating an electric current, which is known as the *streaming current*. On the other hand, the charge transferred downstream generates an electric field in the opposite direction. After a short time, the two currents due to pressure gradient and reverse electric field balance each other. The streaming potential (E_s) is the potential drop associated with this electric field.
- The following equation gives the ζ -potential.

$$\zeta = \frac{\mu k_s}{\epsilon \epsilon_0} \left(\frac{E_s}{\Delta p} \right), \quad \kappa R_c \gg 1 \quad (6)$$

where

k_s is the conductivity of the electrolyte solution.

Equation (6) is valid for the large values of κR_c (where R_c is the radius of the capillary). Therefore, it is likely to give erroneous results when the concentration of salt is low (which would result in a low value of κ).

Determination of ζ -potential from sedimentation potential

- An electric field is developed during the settling of charged particles. This is known as *sedimentation potential*. Smoluchowski presented the first theoretical estimate of the magnitude of the field. For a dispersion of solid non-conducting spheres of radius R_s , immersed in an electrolyte solution of conductivity k_s , dielectric constant ϵ , and viscosity μ , the sedimentation potential is predicted to be;

$$E_{\text{sed}} = \frac{4\pi\epsilon\epsilon_0\zeta\Delta\rho gnR_s^3}{3\mu k_s V_d} \quad (7)$$

where

- n is the number of particles
- V_d is the volume of dispersion.

This equation is valid in those situations where the thickness of electrostatic double layer is small with respect to the radius of the particles ($\kappa R_s \gg 1$). It can be observed from Eq. (7) that the sedimentation potential is proportional to the amount of the dispersed phase.

- The settling of fine droplets can generate high sedimentation potentials. For example, the settling of water drops in the gasoline storage tanks can produce a very high sedimentation potential owing to the low conductivity of the oil phase, which can be dangerous. The value of sedimentation potential can be as high as 1000 V/m or above, even for a moderate value of the ζ -potential (e.g., 25 mV).
- If the diameter of the droplets is larger than 100 μ m, they settle down completely and the sedimentation potential becomes zero. If they are smaller than 1 μ m, the sedimentation potential gradient reduces the rate of settling and a haze of water drops floats in the electric field.

- The sedimentation velocity is reduced by the sedimentation potential gradient. If the steady state settling velocity (i.e., terminal velocity) of the particle is v_t when the particle is uncharged, and v_c is the velocity when the particle carries a surface charge, then for a single sedimenting particle,

$$v_c = v_t \left[1 - \frac{1}{\mu k_s} \left(\frac{\epsilon \epsilon_0 \zeta}{R_s} \right)^2 \right], \quad \kappa R_s \gg 1 \quad (8)$$

- The experimental data agree with this equation within an order of magnitude. If $R_s = 0.1 \mu\text{ m}$, $\zeta = 25 \text{ mV}$ and $k_s = 1 \times 10^{-4} \Omega^{-1} \text{ m}^{-1}$, it can be shown that the velocity of the particle in water will be reduced by 30%. This causes a haze of fine water drops in oil.

A comment on the ζ -potential determined by various methods

- The ζ -potential depends only on the properties of the phases in contact. Therefore, its value must be independent of the experimental method employed for its determination. Several scientists, using the Smoluchowski theory, have found that ζ -potential obtained from streaming potential or electro osmotic measurements is quite smaller than the value obtained from electrophoretic mobility or sedimentation potential measurements.
- These discrepancies can be due to the influence of surface conductivity on streaming potential and electro osmotic flow.
- If the condition $\kappa R \gg 1$ (where R is the radius of sphere, or the radius of capillary) is not satisfied, then the Smoluchowski equation can yield inaccurate values of the ζ -potential.
- Two conditions must be satisfied to justify comparison between the values of ζ -potential obtained by different electro kinetic experiments: the effect of surface conductivity must be taken care of, unless it is negligible, and the surface of shear must divide comparable double layers in all the cases. Fulfillment of the second requirement depends upon the experimental procedure. For example, if the same capillary is used for electro osmosis and streaming potential studies, the second condition can be satisfied. On the other hand, the surfaces of a capillary and a migrating particle can be quite different. Sometimes, the surfaces are coated with a protein, and the characteristics of both surfaces are governed by the adsorbed protein.

Rheology

Rheology is the science of the flow and **deformation** of matter (liquid or “soft” solid) under the effect of an applied force.

- **Deformation** -change of the shape and the size of a body due to applied forces (external forces and internal forces).
- **Flow** - irreversible deformation (matter is not reverted to the original state when the force is removed).
- **Elasticity** - reversible deformation (matter is reverted to the original form after stress is removed).

Factors affecting rheological behaviour of colloidal dispersions

The rheological behaviour of colloidal dispersions depends mainly on the following factors:

1. Viscosity of the dispersion medium.

2. Particle concentration.
3. Particle size and shape.
4. Particle-particle and particle-dispersion medium interactions.

Rheology divided into three sections;

- i. the viscosity of dilute solutions and dispersions
- ii. non-Newtonian flow
- iii. the viscoelastic properties of semi-solid systems

a) Viscosity: Newtonian viscosity

The viscosity of a liquid is a measure of the internal resistance offered to the relative motion of different parts of the liquid. Viscosity is described as Newtonian when the shearing force per unit area τ between two parallel planes of liquid in relative motion is proportional to the velocity gradient D between the planes - i.e. $\tau = \eta D$, where η is the coefficient of viscosity. The dimension of η is, therefore, $(\text{mass}) (\text{length})^{-1} (\text{time})^{-1}$. $\eta = \text{const.}$

Factors affecting viscosity

- pressure
- molecular weight
- temperature
- shear rate or shear stress

Factor which increases entanglements

- branching
- molecular weight
- side groups
- pressure

Any factor which increases entanglements between chains increases the viscosity i.e they affect the ability of the chains to slide past each other.

Newtonian liquids, deform at a rate proportional to the applied stress and show no recovery when the stress is removed, the energy involved having been dissipated as heat in overcoming the internal frictional resistance.

A Newtonian fluid is a fluid whose stress versus rate of strain curve is linear and passes through the origin. The constant of proportionality is known as the viscosity.

b) Non-newtonian viscosity

A non-Newtonian fluid is a fluid whose flow properties are not described by a single constant value of viscosity.

If the relation between shear stress and shear rate is not linear then it is known as *non-newtonian viscosity*. Viscosity varies with the shear: $\eta = f(\tau)$ or $\eta = f(D)$. Most viscous materials are non-newtonian.

Non-newtonian behavior depends on the micro- or nanostructure of the material (breakdown, arrangement, or entanglement).

c) Viscoelasticity

Viscoelastic materials have the following properties;

- i. *Ideally elastic*: Hookean body (only reversible deformation, linear relation between stress and strain).

- ii. *Ideally viscous*: Newtonian fluids (continuous irreversible deformation, flow).

When a typical elastic solid is stressed, it immediately deforms by an amount proportional to the applied stress and maintains a constant deformation as long as the stress remains constant - i.e. it obeys Hooke's law. On removal of the stress, the elastic energy stored in the solid is released and the solid immediately recovers its original shape.

When viscoelastic materials are stressed, some of the energy involved is stored elastically, various parts of the system being deformed into new non-equilibrium positions relative to one another. The remainder is dissipated as heat, various parts of the system flowing into new equilibrium positions relative to one another. If the relative motion of the segments into non-equilibrium positions is hampered, the elastic deformation and recovery of the material is time-dependent (retarded elasticity).

The Weissenberg effect

A characteristic of viscoelastic behaviour is the tendency for flow to occur at right angles to the applied force. An extreme example of this behaviour is illustrated in the figure below.

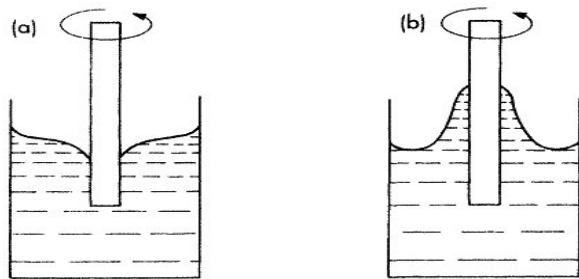


Figure 9.9 The Weissenberg effect: (a) Newtonian liquid; and (b) viscoelastic liquid

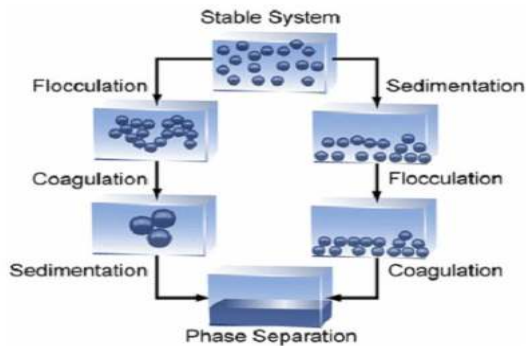
- When a rotating rod is lowered into a *Newtonian liquid*, the liquid is set into rotation and tends to move outwards, leaving a depression around the rod.
- When the rotating rod is lowered into a *viscoelastic liquid*, the liquid may actually climb up the rod. The rotation of the rod causes the liquid to be sheared circularly and, because of its elastic nature, it acts like a stretched rubber band, tending to squeeze liquid in towards the centre of the vessel and, therefore, up the rod.

Applications of Rheology

- Understanding the fundamental nature of a system (basic science).
- Quality control (raw materials and products, processes).
- Study of the effect of different parameters on the quality of a product.
- Tuning rheological properties of a system has many applications in every day's life;
 - Pharmaceuticals
 - Cosmetics
 - Chemical industry
 - Oil-drilling etc

STABILISATION OF COLLOIDS

- A stable colloidal system is one in which the particles resist flocculation or aggregation and exhibits a long shelf-life. Stabilization of colloids depends upon the balance of the repulsive and attractive forces that exist between particles as they approach one another.
- If all the particles have a mutual repulsion then the dispersion will remain stable.
- If the particles have little or no repulsive force then some instability mechanism will eventually take place e.g. flocculation, aggregation etc.



Protection of colloids

Lyophilic sols are more stable than lyophobic sols. Lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to lyophobic sol, the lyophilic particles (colloids) covering up the particles of lyophobic sol.

COAGULATION

The process of setting of colloidal particles is called coagulation or precipitation of the sol.

The coagulation of the lyophobic sols can be carried out in the following ways:-

1. **By electrophoresis:** - The colloidal particles move towards oppositely charged electrodes get discharged and precipitate.
2. **By mixing two oppositely charged sols:** - Oppositely charged sols when mixed almost equal proportional neutralise then changed and get partially or completely precipitated.
3. **By Boiling:** - When a sol is boiled the adsorbed layer is disturbed due to increased collisions with the molecules of the dispersion medium. This reduces the charge on the particles and ultimately led to setting down in the form of a precipitate.
4. **By Persistent dialysis:** - On prolonged dialysis, traces of the electrolyte present in the sol are removed almost completely collides become unstable and ultimately coagulate.
5. **By addition of electrolyte :** - When excess of electrolyte is added the colloidal particles precipitated, the reason is that colloids interact with ions carrying charge opposite to that present on themselves, this causes neutralisation leading to their coagulation.

Coagulation of lyophilic sols:

There are two factors which are responsible for stability of the lyophilic sols. These factors are charge and solvation of the colloidal particles. When these two factors are removed, a lyophilic sol can be coagulated. This is done,

- (i) By addition of an electrolyte
- (ii) By adding a suitable solvent

Hardy-Schulz rules

H. Schulze (1882) and W.B. Hardy (1900) suggested the following rules to discuss the effect of electrolytes of the coagulation of the sol.

- i. Only the ions carrying charge opposite to the one present on the sol. particles are effective to cause coagulation, e.g., the negative charged sol. is best coagulated by cations and a positive sol. is coagulated by anions.
- ii. The charge on coagulating ion influences the coagulation of sol.

In general, the coagulating power of the active ion increases with the valency of the active ion.

After observing the regularities concerning the sign and valency of the active ion, a law was proposed by Hardy and Schulz which is termed as Hardy-Schulze law which is stated as follows: "*Higher is the valency of the active ion, greater will be its power to precipitate the sol.*"

Thus, coagulating power of cations is in the order of $\text{Al}^{3+} > \text{Ba}^{2+}$ or $\text{Mg}^{2+} > \text{Na}^+$ or K^+ .

Similarly, to coagulating the positively charged sol. the coagulating power of anion is in the order of $[\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$

Factors governing coagulation of sols

1. nature of the sol
2. nature of the charge on the sol particles
3. valency of the precipitating ions
4. the mode of defining coagulations
5. time allowed for comparing coagulating concentrations of electrolytes
6. The ratio of surface to mass of dispersed phase. some what larger quantities of precipitants are needed for more concentrated and more finely dispersed sols.
7. Rise temperature favours coagulation.
8. Addition of dehydrants like alcohol induces coagulation of emulsoids.
9. Centrifugal forces greatly enhance the setting out of particles due to a difference in the densities of the medium and the dispersed phase.

Conditions that might cause a colloidal dispersion to coagulate.

- i. *Heating and stirring: increase the frequency and velocity of collisions that are necessary for coagulation to occur.*
- ii. *Addition of an electrolyte: neutralises the surface charges, thus removing the electrostatic repulsion between colloidal particles.*
- iii. *Changing the pH: can flatten / desorb electrosteric stabilisers.*

EMULSIONS

An emulsion is a colloidal dispersion in which both the dispersion medium and dispersed phase are liquids generally; one of the two liquids is water. There are two types of emulsions;

1. ***Oil dispersed in water (O/W type)*** – water act as a dispersion medium. Example: - Milk and vanishing cream.
2. ***Water dispersed in oil (W/O type)*** - oil act as dispersion medium. Example: - Butter and cream.

Detection of type of an emulsion

Various methods of emulsions to test the type of emulsion are as follows:

a) Microscopic methods:

To a small amount of the given emulsion, a few drops of water are added. The water will mix completely if the emulsion is oil-in-water type. Similarly for the water-in-oil emulsions, the miscibility with a few drops of oil can be tested. The miscibility can be seen under a microscope.

b) Conductive method:

This method is based upon adding a small amount of an electrolyte to the emulsion. Of the conductance increases, the emulsion is oil-water type and if there is no significant change; it is water-in-oil type.

c) Dye method:

A small amount of an oil soluble dye is added to the emulsion. If it is water-in-oil type, it becomes deeply colored, otherwise it remains colorless.

Method of preparation of emulsions

An emulsion is prepared by shaking strongly the mixture of the two liquids or by passing the mixture through a colloid mill known as the homogenizer. The emulsions thus prepared from the pure liquids are usually not stable and the two liquids separate out on standing. To get a stable emulsion, small quantities of certain other substances are added during preparation. The substances thus added to stabilize the emulsions are called emulsifiers or emulsifying agents. The substances commonly used as emulsifying agents are soaps of various kinds, long chain sulphonic acids or lyophilic colloids like proteins, gum, and agar.

Properties of emulsions:

- i. Emulsions exhibit all the properties like Tyndall effect, Brownian movement, Electrophoresis, Coagulation on addition of electrolytes.
- ii. The size of the dispersed particles in emulsion is larger than those in the sols. It ranges from 1000 Å to 10,000 Å.
- iii. Emulsions can be broken to yield the constituent liquids by heating, centrifuging by adding larger amounts of the electrolytes to precipitate out the dispersed phase or by chemical destruction of the emulsifying agent. The separation of cream from milk is a well known example of centrifuging.

Factors favouring emulsion stability:

The factors depend on the nature of the emulsifying agent and/or on a suitable choice of formulation and manufacturing conditions.

1. *Low interfacial tension* The adsorption of surfactant at oil-water interfaces causes a lowering of interfacial energy, thus facilitating the development and enhancing the stability of the large interfacial areas associated with emulsions.

2. *A mechanically strong and elastic interfacial film* This is particularly important when the volume fraction of the dispersed phase is high. The stability of emulsions stabilised by proteins arises from the mechanical protection given by the adsorbed films around the droplets rather than from a reduction of interfacial tension. Finely divided solids for which the contact angle is between 0° and 180° have a tendency to collect at the oil-water interface, where they impart stability to the emulsion.

Surfactants can also stabilise in the mechanical sense. Coalescence involves droplet coagulation followed by a squeezing of film material from the region of droplet contact, and the latter is more favoured with an expanded film than with a close-packed film. For example, very stable hydrocarbon oil in water emulsions can be prepared with sodium cetyl sulphate (dissolved in the water) plus cetyl alcohol (dissolved in the oil) as emulsifier (a condensed mixed film being formed at the interface), whereas hydrocarbon oil in water emulsions prepared with sodium cetyl sulphate plus oleyl alcohol (which gives an expanded mixed film) are much less stable. The most effective interfacial films are the mixed films which are formed as a result of the combined use of water-soluble and oil-soluble emulsifying agents. It is also important that the emulsifier films have sufficient elasticity to enable recovery from local disturbances.

3. *Electrical double layer repulsions* Inter particle repulsion due to the overlap of similarly charged electric double layers is an important stabilising mechanism in O/W emulsions. When ionic emulsifying agents are used, lateral electric double layer repulsion may prevent the formation of a close-packed film. This film-expanding effect can be minimised by using a mixed ionic plus non-ionic film (see above) and/or by increasing the electrolyte concentration in the aqueous phase

4. *Relatively small volume of dispersed phase.*

5. *Narrow droplet size distribution;* Larger droplets are less unstable than smaller droplets on account of their smaller area-to-volume ratio, and so will tend to grow at the expense of the smaller droplets. If this process continues, the emulsion will eventually break. Emulsions with a fairly uniform droplet size will be less prone to this effect.

6. *High viscosity;* A high Newtonian viscosity simply retards the rates of creaming, coalescence, etc. If a weak gel network is formed by, for example, dissolving sodium carboxy methyl cellulose in an O/W emulsion, genuine stability might ensue. However, the overall Theological properties of such an emulsion may not be acceptable.

Demulsification (Breaking up of emulsions):

It is the process which involves the breaking of an emulsion into two separate liquid layers. The following methods may be used to bring demulsification:

1. suitable centrifugal action
2. heating under pressure
3. distilling off of one component, usually of water
4. freezing out of a component
5. chemical destruction of the stabilizer
6. extraction of one of the components with the solvent
7. applying a strong electric field (electrophoresis)
8. addition of a suitable electrolyte (coagulation)
9. addition of demulsifiers like alcohol, phenol, turkey red oil
10. addition of a large bulk of the inner phase

Uses of emulsions.

Uses of emulsions are:

- (i) Formation of emulsions determine the cleansing action of the soap.
- (ii) The process of emulsification is responsible for the digestion of fats in intestines.
- (iii) Emulsions are formed on adding antiseptics and disinfectants to water.
- (iv) Emulsification is used to make medicines.

GELS

Colloidal system in which liquids are the dispersed phase and solid act as the dispersion medium are called gels. The common examples are: boot polishes, jelly, gum arabic, agar, processed cheese and silicic acid.

When the gels are allowed to stand for a long time, they give out small quantities of trapped liquids with accumulate on its surface. This action of gels is known as *Synresis* or *Weeping*. Some gels such as silica, gelatin and ferric hydroxide liquify on shaking and reset on allowing to stand. This phenomenon of Sol-gel transformation is called thixotropy.

Gels are divided into two categories i.e. elastic gels and non elastic gels. The two categories differ from their behaviour towards dehydration and rehydration as under.

<i>Elastic gels</i>	<i>Non-elastic gels</i>
1. They change to solid mass on dehydration which can be changed back to original form by addition of water followed by warming.	1. They change to solid mass on dehydration which cannot be changed back to original form with water.
2. They absorb water when placed in it simultaneous swelling. This phenomenon is called imbibation.	2. They do not exhibit imbibation.

FOAMS

Foams are dispersions of gas bubbles in a liquid which is in the continuous phase. The diameters of the foam bubbles range from about 1 micrometer to several centimeters. Depending on the bubble size and wall thickness, dense or light foams are formed. Food foams contain large amounts of entrapped gas.

Formation of foams:

Liquid capable of forming foams have low surface tension and thus can spread or stretch easily and so not coalesce readily. They also must have low vapor pressure. For the formation of a foam there must be a foaming agent in the continuous phase prior to dispersion of gas. The foaming agent must be absorbed at the surface to reduce surface tension and provide a distinct surface layer which resists the coalescence of gas bubbles. Surface active lipids, glycosides, cellulose derivatives and protein are used as foaming agents.

Antifoaming agents

Several liquids will destroy foams; ether, toluene, the aliphatic alcohols, and some oil breaks most foams.

Foams can often be broken by spraying with small quantities of substances such as ether and n-octanol. As a result of their high surface activity, these foam breakers raise the surface pressure over small regions of the liquid films and spread from these regions, displacing the foaming agent and carrying with them some of the underlying liquid. Small regions of film are, therefore, thinned and left without the properties to resist rupture.

Foam stability:

Foam stability can be enhanced by increasing the elasticity of the bubble walls, by increasing the viscosity of the solution. And this can be done by introducing gums and proteins, such as gelatin. Foaming agents also helps in the stability of foam. Protein coagulum has a high water binding capacity and thus contributes to a decrease in the rate of drainage from foam.

Stabilization Mechanisms of foams

Practical mechanisms for extending the persistence of foams can include one or several of the following conditions:

- i. A high viscosity in the liquid phase, which retards hydrodynamic drainage, as well as providing a cushion effect to absorb shocks resulting from random or induced motion;
- ii. A high surface viscosity, which also retards liquid loss from between interfaces and dampens film deformation prior to bubble collapse;
- iii. Surface effects such as the Gibbs and Marangoni effects, which act to “heal” areas of film thinning due to liquid loss;
- iv. Electrostatic and steric repulsion between adjacent interfaces due the adsorption of ionic and nonionic surfactants, polymers, and other agents, which can oppose drainage through the effects of the disjoining pressure;
- v. Retardation of gas diffusion from smaller to larger bubbles.

The addition of surfactants and/or polymers to a foaming system can alter any or all of the above-mentioned system characteristics and therefore enhance the stability of the foam. They may also have the effect of lowering the surface tension of the system, thereby reducing the work required for the initial formation of the foam, as well as producing smaller, more uniform bubbles.

APPLICATIONS & USES OF COLLOIDS

Colloids are widely used in the industrial sector.

(1) **Medicines** : The medicines containing gold, silver or calcium etc. in colloidal form are more effective and easily assimilated by the human systems.

(2) **Dyes**: In dyeing, mordants colloidal substances are used in textile dyeing industry to fasten dyes.

(3) **Rubber industry**: Latex is a colloidal solution of negatively charged particles. The article to be rubber plated is made the anode. Under the influence of electric field the rubber particles get deposited on the anode and the article gets rubber plated.

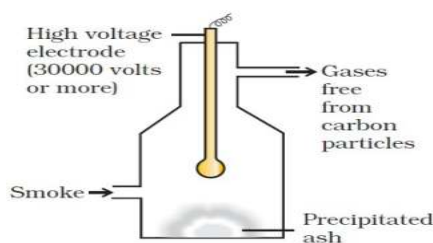
(4) **Smoke screens**: Smoke screens which consist of titanium dioxide dispersed in air are used in warfare for the purpose of concealment and camouflage.

(5) **Formation of delta** : The river water carries with it charged clay particles and many other substances in the form of colloidal solution. When the sea water comes in contact with these particles, the colloidal particles in river water are coagulated by the electrolytes present in sea water to form deltas.

(6) **Purification of water** : The turbidity in water is due to the presence of negatively charged clay particles. The addition of potash alum, i.e., Al^3 ions neutralizes the negative charge on the colloidal particles and thus causes their coagulation. The coagulated matter settles down and thus becomes clear.

(7) **Artificial rain** : Artificial rain can be caused by throwing electrified sand on clouds which are colloidal solutions or charged particles of water in air.

(8) **Smoke precipitation** : Smoke coming out of the chimney in industrial area is a nuisance and health hazard. It is a colloidal particles are charged particles and thus they are removed from fuel gases by electrical precipitation (Cottrell Precipitator).



In cottrell precipitator, the smoke is made to pass through chambers fitted with highly electrically charged plates which precipitate the carbon and dust particles leaving in the gases to escape through chimney (figure).

(9) ***Sewage disposal*** : Sewage water consists of particles of dirt, rubbish, mud, etc., which are of colloidal dimensions and carry an electric charge and thus do not settle down easily. These particles can thus be removed by cataphoresis. A system of two tanks fitted with metallic electrodes is used for this purpose. When electric field is created, then the dust particles are coagulated on the oppositely charged electrodes. The deposit may be utilized as a manure.

(10) ***Cleansing action of soap and detergent*** : Soap solution may be used to wash off the dirt sticking to the fabric, in the presence

- i. If forms a colloidal solution in water forms (miscelles), removes dirt by simple adsorption of oily substance and thus washes away.
- ii. It decreases the interfacial tension between water and grease, and it causes the emulsification of grease in water. By mechanical action such as rubbing, the dirt particles are also detached along with the oily material.

(11) ***Most of our food has colloidal nature***

Important examples of such foods are milk, ice-cream, butter, fruit jellies etc.

(12) ***In Photography*** : Various colloidal system are used in photographic process. In the preparation of photographic plates, the silver bromide in gelatin is coated on thin glass plates. In developing and fixation, various colloidal substances are used. In different kinds of colour printing, gelatin and other colloidal mixtures are used.

(13) ***Blue colour of the sky*** : Colloidal particles scatter only blue light and the rest of is absorbed. In sky there are a number of dust and water particles. They scatter blue light and, therefore, sky looks bluish. If there were no scattering, the sky would have appeared totally dark.

Exercise

Exercise 1.4.1: Calculate the sedimentation potential for 50 μm radius water drops in an oil (dielectric constant = 2, viscosity = 0.5 mPa s, and conductivity = $1 \times 10^{-9} \Omega^{-1} \text{m}^{-1}$) if the ζ -potential is 0.025 V. The density of the oil is 700 kg/m³ and the volume fraction of the dispersed aqueous phase is 0.05.

Exercise 1.4.2: Calculate the electrophoretic mobility of a 50 nm diameter spherical colloid particle in an aqueous solution of NaCl at 298 K. The ζ -potential is 0.02 V. The concentration of NaCl in the solution is 100 mol/m³. Given: The Debye length is ~ 1 nm at this concentration of the salt.

Exercise 1.4.3: Application of 101.325 kPa pressure produces a streaming potential of 0.4 V in an experiment using aqueous NaCl solution. Calculate the ζ -potential. Given: $k_S = 0.01 \times 10^{-9} \Omega^{-1} \text{m}^{-1}$ and $\mu = 1 \text{ mPa s}$.

$$\zeta = \frac{\mu k_S}{\epsilon \epsilon_0} \left(\frac{E_s}{\Delta p} \right), \quad \kappa R_\zeta \gg 1$$

Exercise 1.4.4: Answer the following questions clearly.

- What are the advantages and limitations of transmission electron microscopy in the characterization of colloidal materials?
- What are the different types of signals produced in a scanning electron microscope?
- Explain how dynamic light scattering can be used to measure the size of a colloid particle.
- For what types of colloids does the dynamic light scattering have advantage over TEM or SEM?
- What are the advantages of neutron scattering over visible light scattering? What is small-angle neutron scattering? Where is it used?
- Explain what you understand by electro kinetic phenomena.
- What are the four major electro kinetic phenomena?
- Explain electrophoresis. What are the major uses of electrophoresis?
- What is zeta potential? Explain its significance.
- Discuss the applicability criteria of Hückel and Smoluchowski equations.
- What is electro osmosis? How does it differ from osmosis? What is electro osmotic pressure?
- Explain how you would calculate the zeta potential from electro osmosis.
- What is streaming potential? How is it developed?
- What is sedimentation potential?

Question

2. In an electrophoresis experiment, spherical colloidal particles of diameter 0.5 μm are dispersed in a solution of 0.10 mol/L NaCl. If the particles are observed to cover a distance of 120 μm in 5.0 s, under a potential gradient of 10.0 V/cm, calculate: [14 marks]
- the electrophoretic mobility of the particles;
 - an estimate of the zeta potential (ζ) of the particles;
 - an estimate of the charge density at the surface of shear;
 - an estimate of the error in the electrophoresis measurement arising from the Brownian displacement of the particle that occurs during the experiment.

Electrophoretic mobility = Distance(metres) x time (sec)/potential gradient (V/m)

- a) check κa
 $\kappa a = k \times r$

$$\kappa a = 3.29 \times 10^9 (0.10 \text{ M} \times 10^{-2})^{1/2} \text{ m}^{-1} \times 0.25 \times 10^{-6} \text{ m} = 260$$

\therefore Smoluchowski equation is valid

$$u_E = \frac{v_E}{E} = \frac{120 \times 10^{-6} \text{ m} \times 5.0 \text{ s}}{10.0 \frac{\text{V}}{\text{cm}} \times 100 \frac{\text{cm}}{\text{m}}} = 2.4 \times 10^{-8} \frac{\text{m}^2}{\text{Vs}}$$

- b) Using the Smoluchowski equation

$$\zeta = \frac{\eta u_E}{78.5 \epsilon_0} = \frac{0.891 \times 10^{-3} \text{ Pa s} \times 2.4 \times 10^{-8} \frac{\text{m}}{\text{s}}}{78.5 \times 8.854 \times 10^{-12} \frac{\text{F}}{\text{m}}} = 0.0308 \text{ V} = 30.8 \text{ mV}$$

- c)

$$C_2 = \frac{\sigma_0}{\psi_d} \quad (\text{note : assume } \psi_d = \zeta)$$

$$C_2 = \frac{\sigma_0}{\zeta} \Rightarrow C_2 \times \zeta = \sigma_0$$

$$\sigma_0 = 2.28 (0.10)^{1/2} \frac{\text{F}}{\text{m}^2} \times 0.0308 \text{ V} = 0.0222 \frac{\text{C}}{\text{m}^2}$$

- d)

$$\bar{x} = (2Dt)^{1/2}$$

$$D = \frac{k_B T}{6\pi\eta a} = \frac{1.381 \times 10^{-23} \frac{\text{J}}{\text{K}} \times 298 \text{ K}}{6\pi \times 0.891 \times 10^{-3} \text{ Pa s} \times 0.25 \times 10^{-6} \text{ m}} = 9.81 \times 10^{-13} \frac{\text{m}^2}{\text{s}}$$

$$\therefore \bar{x} = (2Dt)^{1/2} = \left(2 \times 9.81 \times 10^{-13} \frac{\text{m}^2}{\text{s}} \times 5.0 \text{ s} \right)^{1/2} = 3.13 \times 10^{-6} \text{ m}$$

$$\% \text{ error} = \frac{3.13 \times 10^{-6} \text{ m}}{120 \times 10^{-6} \text{ m}} \times 100\% = 2.61\%$$

Important Questions of Surface Chemistry and Colloids

1. Explain the difference between absorption and adsorption. Discuss the types of adsorption isotherms.
2. Write notes on the following:
 - (a) Freundlich adsorption isotherms.
 - (b) Langmuir adsorption isotherms.
3. What do you understand by the colloidal state of matter? Bring out the difference between a colloidal solution and a true solution.
4. Describe the general methods for the preparation of colloids. Give one example for each method.
5. Explain the use of (a) dialysis (b) electro-dialysis (c) ultrafiltration.
6. Distinguish between lyophobic and lyophilic colloids.
Describe Bredig's arc method for the preparation of lyophobic colloids.
7. Give an account of the applications of colloids.
8. Write notes on the following:
 - (a) Artificial rain.
 - (b) Cottrell smoke precipitator.
 - (c) Tyndall effect.
9. How would you determine;
 - (a) Colloidal solution is brought under influence of an electric field.
 - (b) A beam of light is passed through a colloidal solution.
 - (c) Colloidal solution has very low osmotic pressure than the true solution, why?

