Physical Pharmacy II
2nd stage
College of Pharmacy

lec: 7
Interfacial Phenomena (part 1)

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Interfacial Phenomena

- When two different phases come into contact (for example: oil and water, air and water, or a solid and a liquid), the boundary between them is called an **interface**.
    - At this boundary, **molecules behave differently** compared to those inside each phase.
- This special behavior is called **interfacial phenomena**.
- Molecules at the interface are **not surrounded equally** like those inside the bulk.
    - This causes **unique properties**, such as:
        - **Surface tension**
        - **Adhesion**
        - **Wetting**

- **Several types of interface** can exist, depending on whether the two adjacent phases are in the solid, liquid, or gaseous state as shown in the table
- For convenience, these various combinations are divided into two groups:
  1. **Liquid Interfaces:** These involve a **liquid** with:
     - Gas → (e.g., water surface exposed to air)
     - Another liquid → (e.g., oil and water)
  2. **Solid Interfaces:** These involve a **solid** with:
     - Gas → (e.g., tablet exposed to air)
     - Liquid → (e.g., a solid dissolving in water)
     - Another solid → (e.g., the adhesion between granules, the preparation of layered tablets, and the flow of particles)
- **Surface:** The term **surface** is commonly used when **A gas is one of the phases**
  - Examples:
    - The top of a liquid → **gas–liquid interface**
    - A rain droplet → surface between **water and air** constitutes **a gas–liquid interface**
    - a table top surface forms a **gas–solid interface** with the atmosphere above it

Classification of Interfaces		
Phase	**Interfacial Tension**	**Types and Examples of Interfaces**
Gas–Gas	—	No interface possible
Gas–liquid	γ_{LV}	Liquid surface, body of water exposed to atmosphere
Gas–solid	γ_{SV}	Solid surface, table top
Liquid–liquid	γ_{LL}	Liquid–liquid interface, emulsion
Liquid–solid	γ_{LS}	Liquid–solid interface, suspension
Solid–solid	γ_{SS}	Solid–solid interface, powder particles in contact

where the subscript

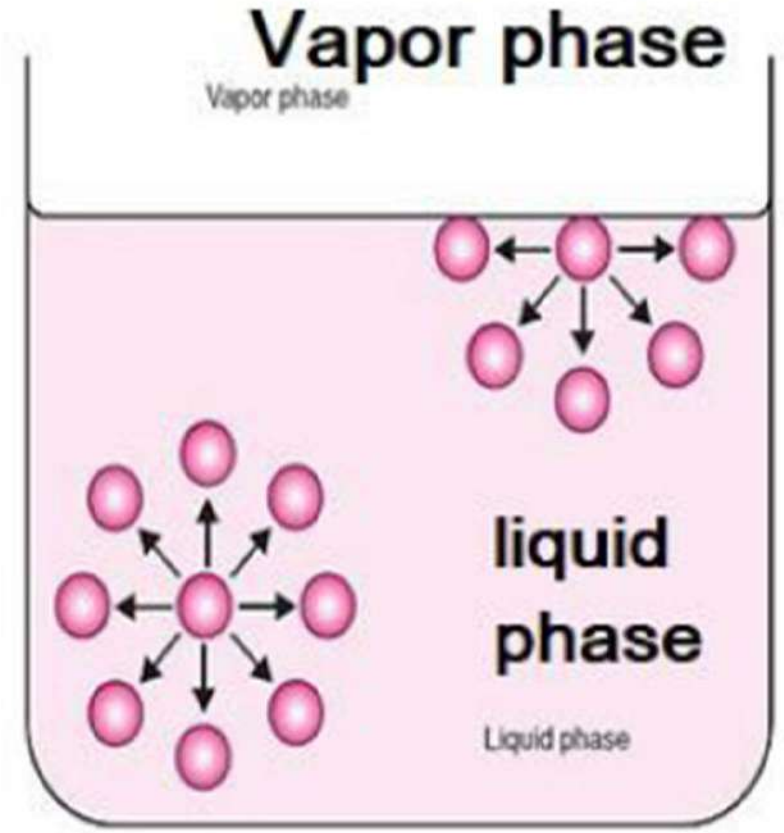
- **L stands for liquid**
- **V for vapor or gas**
- **S for solid**

Liquid Interfaces

Surface and Interfacial Tensions

Surface tension is a property that makes the surface of a liquid behave almost like a stretched elastic sheet**.**

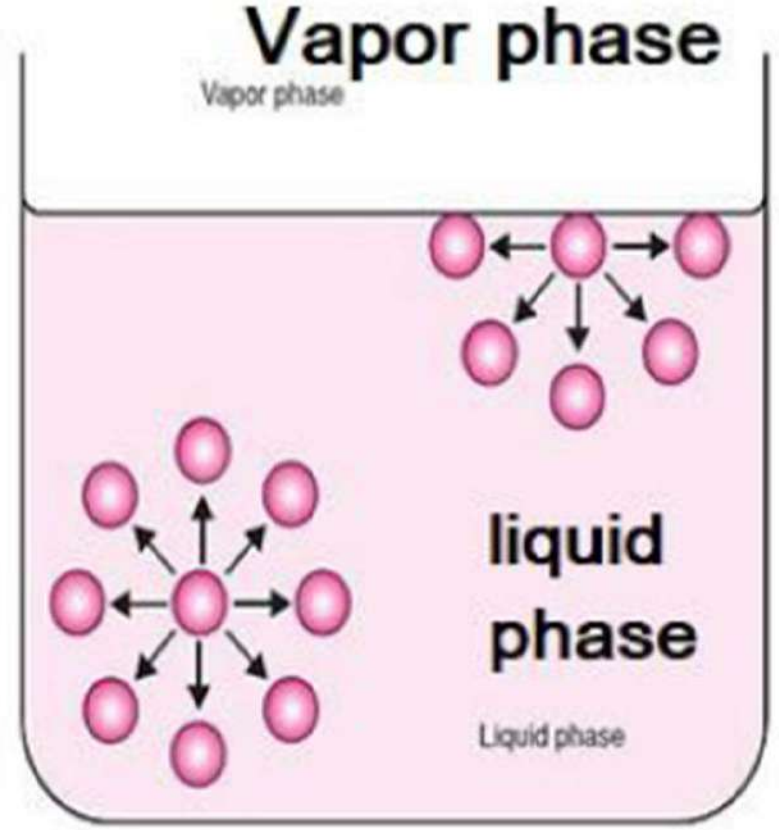
- It is caused by the **attraction between molecules** of the liquid by various intermolecular forces.
  - In the liquid state, the cohesive forces between adjacent molecules are well developed.
  - **Molecules in the bulk** liquid are surrounded in all directions by other molecules for which they have an equal attraction.
  - On the other hand, **molecules at the surface** (i.e., at the liquid–air interface) can only develop attractive cohesive forces with other liquid molecules that are situated below and adjacent to them.



Liquid Interfaces

Surface tension

- **Molecules at the surface** are not surrounded on all sides—they have neighbors beside and below them, **but not above** (if the surface is exposed to air).
- They can develop **adhesive forces of attraction** with the molecules constituting the other phase involved in the interface, this adhesive force of attraction is small.
- The net effect is that the molecules at the surface of the liquid experience an **inward force toward the bulk**, as shown in the Figure.
- Such a force pulls the molecules of the interface together and, **as a result**, contracts the surface, resulting in a surface tension.
- Unequal attractive forces acting on molecules at the surface of a liquid as compared with molecular forces in the bulk of the liquid



Interfacial tension

- **Interfacial tension** Is the force per unit length existing at the interface between **two immiscible liquid phases** and, like surface tension, has the **units of dynes/cm**.
- Ordinarily, **interfacial tensions** are **less than surface tensions** because the adhesive forces between two liquid phases forming an interface are **greater** than when a liquid and a gas phase exist together.
- If two liquids are **completely miscible**, **no interfacial tension** exists between them.
- **The values for surface tension** reflect the **nature of intermolecular** forces present.
  - Large values for **mercury** (metallic bonds) and **water** (H-bond) and the lower values for **benzene** and **chloroform** (London forces)
- **Values of interfacial tensions** reflects the **differences in chemical structure of the two phases** involved, the greater the tendency to interact, the less interfacial tension.
  - In each case the **presence** of chemical groups capable of hydrogen bonding with water markedly decrease interfacial tension.

- Some representative surface and interfacial tensions are listed in the following table

Surface Tension and Interfacial Tension (Against Water) at 20°C			
Substance	**Surface Tension (dynes/cm)**	**Substance**	**Interfacial Tension (dynes/cm)**
Mercury	476	Mercury	375
Water	72.8	Water	-------
Glycerin	63.4	Glycerin	Zero (miscible liquids)
Oleic acid (Carboxylic acid)	32.5	Oleic acid	15.6
Benzene	28.9	Benzene	35.0
Chloroform	27.1	Chloroform	32.8
Olive oil (Oleic acid is the chief constituent)	35.8	Olive oil	22.9
Octanol (alcohol)	26.5	Octanol	8.5

- Interfacial tension causes immiscible liquids to **resist mixing**.
  - Oil and water do not mix because of interfacial tension.
- To dispense one in the other, it is necessary to introduce another kind of molecule that has **affinity** for both **oil and water** like an amphiphile molecule.
- This type of molecule is called **surface active agent (S.A.A**).
  - These molecules when place them at the interface of oil and water will **decrease** the **interfacial tension**, allowing oil and water to mix.
- Both **Surface and interfacial** tensions **decrease by increasing the temperature**, due to increase in the kinetic energy of the molecules.
- They are also **decrease** by addition of S.A.A

Surface free energy

- Each molecule near the surface of liquid possesses a certain excess of potential energy as compared to the molecules in the bulk of the liquid Because they are less stable than molecules inside the liquid.
- **The higher the surface area** of the liquid, the more molecules have this excessive potential energy.
- Therefore, **if the surface of the liquid increases** (e.g., when water is broken into a fine spray), the **energy of the liquid also increases**.
  - Because this energy is proportional to the size of the free surface, it is called a **surface free energy**.
- Therefore, **Surface free energy** can be defined as the **work that must be done to increase the surface by unit area.**
  - As a result of such an expansion, more molecules must be brought from the bulk to the interface.
  - The **more work** that has to be expended to achieve this, the **greater is the surface free energy**.
  - The liquid takes form with minimal free surface and with minimal surface energy.
    - For example, liquid droplets tend to assume a spherical shape because a sphere has the smallest surface area per unit volume.

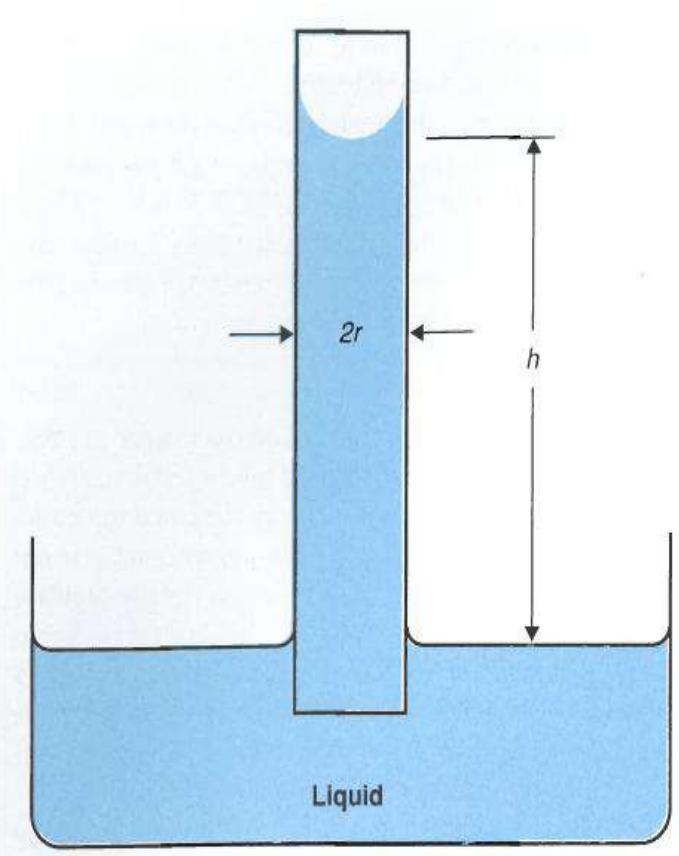
Measurement of Surface and Interfacial Tensions

- Among the several methods that exist for obtaining **surface and interfacial tensions**, only the **capillary rise and the DuNo¨uy ring methods**
- The choice of a particular method often depends on
  - whether surface or interfacial tension is to be determined
  - the accuracy and convenience desired
  - the size of sample available
  - whether the effect of time on surface tension is to be studied

Measurement of Surface and Interfacial Tensions

Capillary Rise Method

- When a **capillary tube** is placed in a liquid contained in a beaker, the liquid generally **rises up** the tube a certain distance.
- Because the force of **adhesion** between the liquid molecules and the capillary wall is **greater than the cohesion** between the liquid molecules, the liquid is said to wet the capillary wall, spreading over it and rising in the tube.
- By measuring this **rise in a capillary**, it is possible to determine the **surface tension** of the liquid.
- It is **not possible**, however, to obtain interfacial tensions using the **capillary rise method**.
- Consider a capillary tube immersed in a liquid that wets its surface, as seen in Figure below.
- Because of the surface tension, the liquid continues to rise in the tube, but because of the weight of the liquid, the upward movement is just balanced by the downward force of gravity



$$\gamma = \frac{1}{2} rh\rho g$$

where **r** is the inside radius of the tube, **h** is the height of the liquid inside the tube, **ρ** is the density of the liquid, **g** is the acceleration due to the gravity

Example :

A sample of chloroform rose to a height of 3.67 cm at 20◦C in a capillary tube having an inside radius of 0.01 cm. What is the surface tension of chloroform at this temperature? The density of chloroform is 1.476 g/cm3.

We write

$$\gamma = \frac{1}{2} rh\rho g$$

$$\gamma = \frac{1}{2} \times 0.01 \text{ cm} \times 3.67 \text{ cm} \times 1.476 \text{ g/cm3} \times 981 \text{ cm/sec2}$$

$$\gamma = 26.6 \text{ g/sec2} = 26.6 \text{ dynes/cm}$$

The DuNo¨uy Ring Method

- The DuNo¨uy tensiometer is widely used for measuring **surface and interfacial tensions**.
- It is an experimental method that uses a **thin metal ring** (usually made of platinum–iridium) to measure how strongly molecules at a liquid's surface hold together.

Basic Principle

- When the ring is placed on the liquid surface and then **pulled upward**, the liquid resists being separated.
- The **force required to detach the ring** from the surface or interface is directly related to the **surface tension** (or **interfacial tension** if two liquids are involved).
- The force required to detach the ring in this manner is provided by a torsion wire and is recorded in dynes on a calibrated dial.

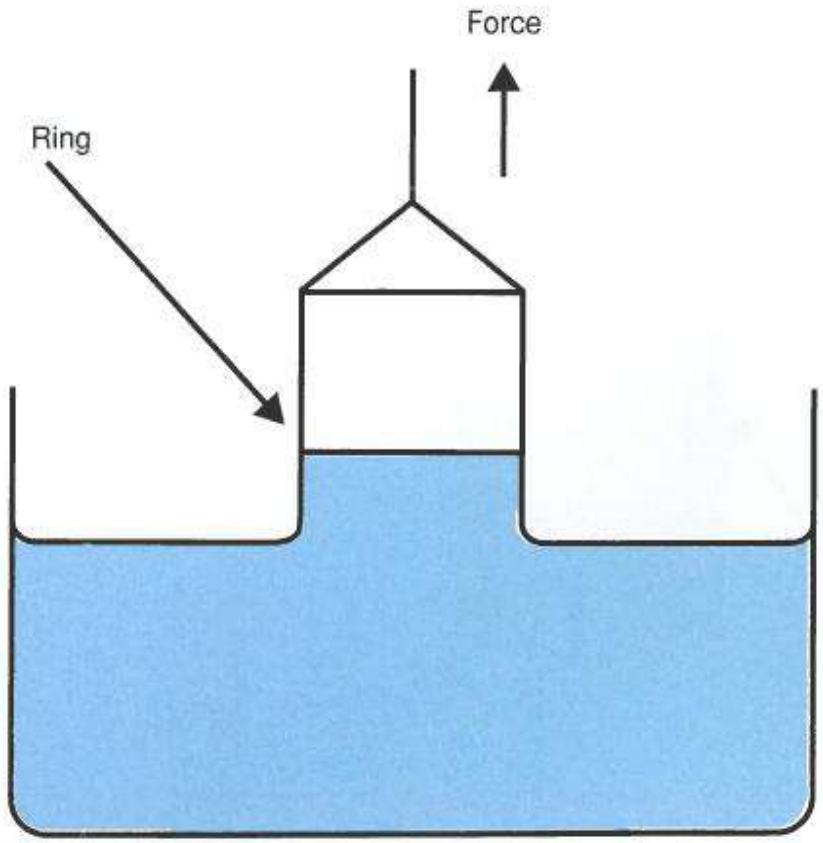


FIG. 15-6 Schematic of the tensiometer ring pulling a column of water above the surface before it brakes away.

Spreading Coefficient

- **Lotions, creams, sunscreens**, and many cosmetics have to be **spread** on the skin to exert their effect.
- When a **liquid** spreads over the **surface of a substrate**, it covers all or a part of the surface.
- **The substrate** can be a **solid** or another **liquid that is immiscible** with the spreading liquid.
- When a **drop of oil** is added on the surface of **water**, three things may happen:
  1. The drop may spread as **a thin film** on the surface of water.
  2. It may form a **liquid lens** if the oil **cannot spread** on the surface of water.
  3. The drop may spread as **a monolayer film** with areas that are identified as lenses
- Spreading **depends** on the **surface tension of the liquids** involved and on the **interfacial tension between them**, that is mean spreading depends on **the force of cohesion and adhesion**.
- For example : oleic acid is placed on the surface of water, it will spread as **a film** if the force of adhesion between the oleic acid molecules and the water molecules is greater than the cohesive forces between the oleic acid molecules themselves.



A. Formation of a lens when a drop of oil is added to water.

B. Monolayer of oil with a lens.

Spreading Coefficient

- Since spreading is dependent on the forces of adhesion and cohesion which means it **depend on work of adhesion and work of cohesion.**
- **Work of adhesion :-** is the energy required to **break the attraction** between the **unlike molecules**. OR to separate two **immiscible liquids** that form an interface
- **The work of adhesion** is equal to the **newly** created surface tensions, **γL** and **γS**, minus the **interfacial tension, γLS**, that has been destroyed in the process.
- The work of adhesion is thus
- **$W_a = \gamma_L + \gamma_S - \gamma_{LS}$**

Wa : **work of adhesion** (attraction between oil and water)
γS: surface tension of **water (subphase)**
γL : surface tension of spreading liquid (**oil)**
γLS : **interfacial tension** between liquid (oil) and water.

- **The work of cohesion**: is the work required to separate the molecules of the spreading liquid so that it can flow over the substrate

$W_c = 2\gamma_L$

Wc = **work of cohesion** (attraction within the oil itself)

- For spreading to occur the **work of adhesion** should be greater than the **work of cohesion**

  Wa- Wc= S (S is known as **spreading coefficient)**

OR

S = Wa- Wc

= (γL + γS – γLS) - 2 γL

=γL + γS – γLS - 2 γL

= γS – γLS – γL

S = γS- (γL +γLS)

- **S** = **+ve** value the liquid **spread** as a film
- **S** = **-ve** value the liquid form **globules** or **floating lens** and **fail** to spread over the liquid

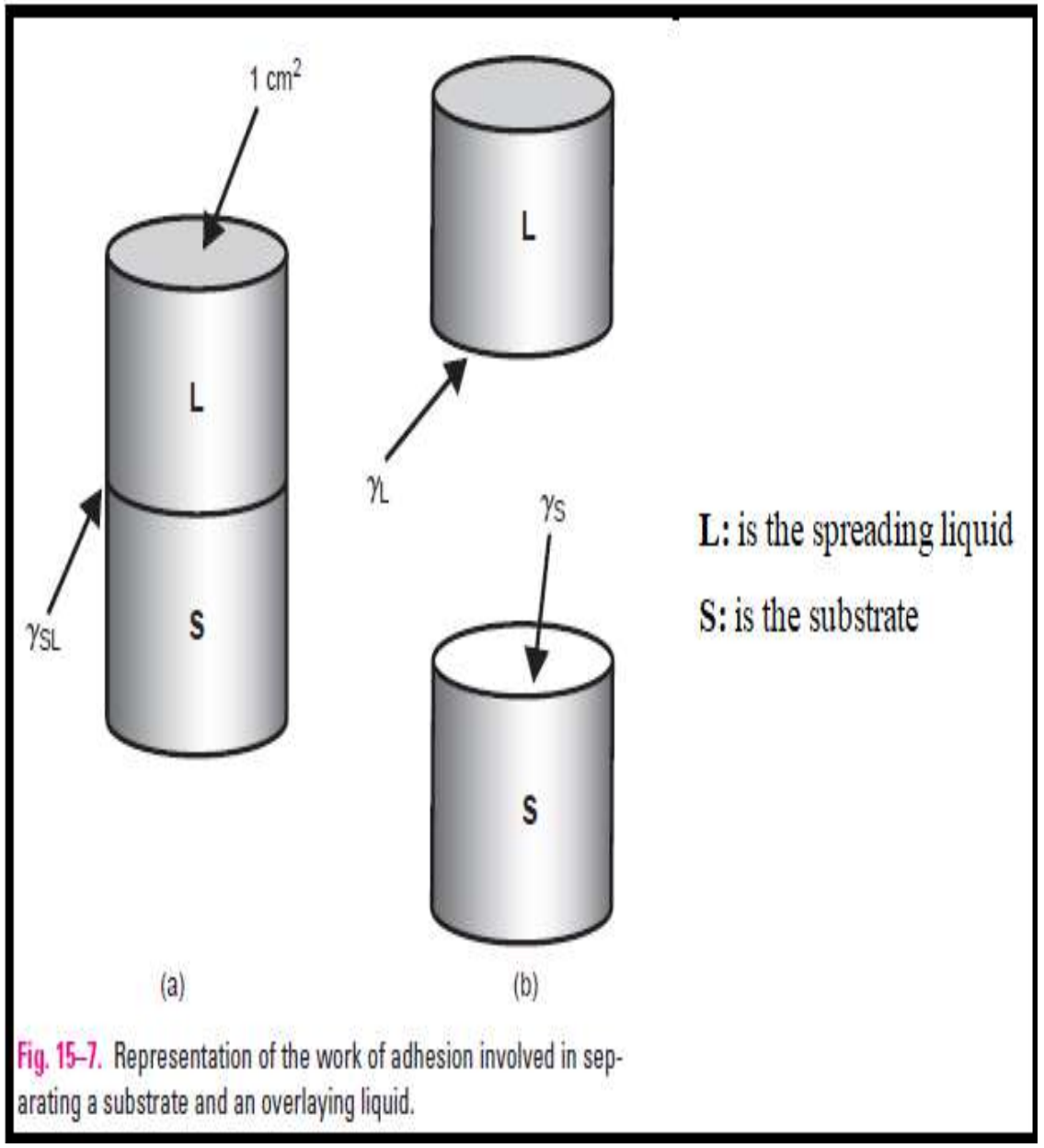


Fig. 15–7. Representation of the work of adhesion involved in separating a substrate and an overlaying liquid.

Example : Which liquid is spread over the other?

γHexane = 18 dyne/cm

γwater = 72.8dyne/cm

γHexane/water= 50.8

If we want to spread hexane over water

$S = \gamma S - (\gamma L + \gamma LS)$

$S = 72.8 - (18+50.8)$

S= **4.0** dyne/cm

If we want to spread water over hexane

$S = \gamma S - (\gamma L + \gamma LS)$

$S = 18 - (72.8+50.8)$

S= **- 105.6** dyne/cm

- Therefore the fact that both liquids are the same, the **high surface tension of water** prevent its spreading over hexane, while **hexane** with low surface tension and low cohesive forces can spread over water

Home Work

If you know that

γ water **=** 72.8 dyne **/**cm

γ oleic acid **=** 32.5 dyne/cm

γ water/ oleic acid=15.6dyne/cm

Which liquid can spread over the other ? Explain

- **Sometimes spreading** will **occur only initially**, and later the spreading liquid will be converted and a **lens will form.**
- The conversion of the liquid to a lens occurs because the *two substances in contact with each other become mutually saturated and their respective surface tensions become different from the initial surface tensions* (when the liquids were pure).
- If we use **a prime (′)** to denote the values **following equilibration** (saturation) (i.e., final rather than initial values) , then the **new surface tensions** are **$\gamma S'$** and **$\gamma L'$**.
  - **When mutual saturation** has taken place, the ***spreading coefficient*** *may be* ***reduced or may even become negative***

Example 16-7 :

- If the surface tension of water γS is 72.8 dynes/cm at 20°C, the surface tension of benzene, γL, is 28.9 dynes/cm, and the interfacial tension between benzene and water, γLS, is 35.0 dynes/cm, what is the **initial** spreading coefficient? Following equilibration, **γS′ is 62.2** dynes/cm and **γL′ is 28.8** dynes/cm. What is the **final** spreading coefficient?

  S = γS- (γL +γLS)

  S = 72.8- (28.9 + 35)

  S = 8.9 dyne/cm

  After equilibrium

  S′ = γS′ - (γL′+γLS)

  S\ = 62.2 – (28.8+35)

  = - 1.6 dyne/cm

- Therefore when benzene is added to water, one will observe an **initial rapid spreading of benzene on the surface of the water**, but later when benzene and water become mutually saturated with each other, **the benzene retracts and forms a lens**
- *In the case of **organic liquids** spread on water, it is found that although the initial spreading coefficient may be **positive or negative**, the **final** spreading coefficient **always has a negative value***
- It is important to consider the types of molecular structures that lead to high spreading coefficient.

- **A material spreads** over water because it contains **polar groups** such as COOH or OH.
- But the carbon chain, **increases**, the **ratio** of polar–nonpolar character **decreases** and the **spreading coefficient on water decreases.**
- Many nonpolar substances, such as liquid petrolatum (S = -13.4), fail to spread on water.
- **Benzene** spreads on water **not** because it is **polar** but because the **cohesive forces** between its molecules are **much weaker than the adhesion for water**
- **Surface active agents** (SAA) **increase S** because they **interfere with cohesive forces**

Initial Spreading Coefficient, S, at 20°C	
Ethyl alcohol	50.4
Propionic acid	45.8
Ethyl ether	45.5
Acetic acid	45.2
Acetone	42.4
Undecylenic acid	32 (25°C)
Oleic acid	24.6
Chloroform	13
Benzene	8.9
Hexane	3.4
Octane	0.22
Ethylene dibromide	-3.19
Liquid petrolatum	-13.4

Adsorption at Liquid Interfaces

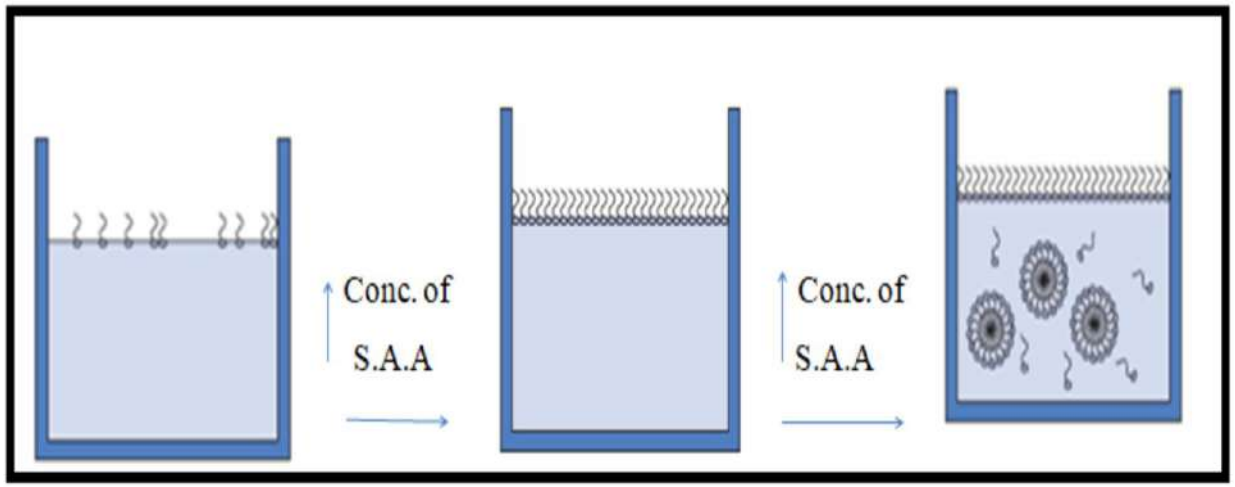
- **Adsorption** is a spontaneous phenomenon where the added **molecules** are partitioned in favor of the interface, adsorption can occur at the **surface or interfaces** of liquid with other liquids (***positive adsorption***).
- It is the **amphiphilic nature** of **surface-active agents** that causes them to be adsorbed at interfaces, whether these are liquid–gas or liquid–liquid interfaces.
- For the amphiphile to be **concentrated at the interface**, it **must be balanced with the proper amount of polar and nonpolar groups.**
  - If the molecule is **too hydrophilic**, it **remains** within the body of the **aqueous phase** and exerts **no effect at the interface.**
  - Likewise, if it is **too lipophilic**, it **dissolves** completely **in the oil** phase and **little appears at the interface**
- Other materials (e.g., inorganic electrolytes) are **partitioned** in favor of the **bulk**, leading to ***negative adsorption*** and a corresponding increase in surface free energy and surface tension.

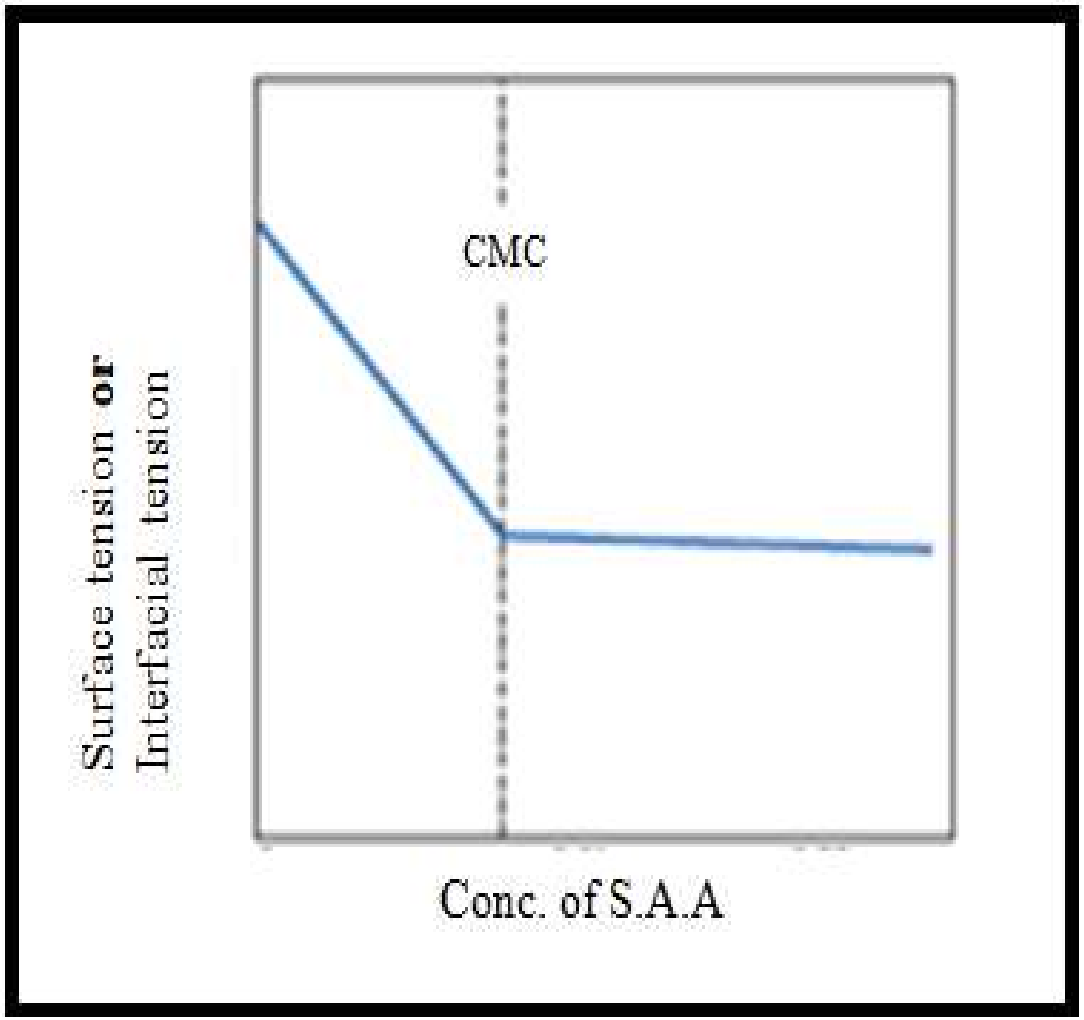
Surface active agents

➢ *Effect of Surface active agents on surface and interfacial tension of water*

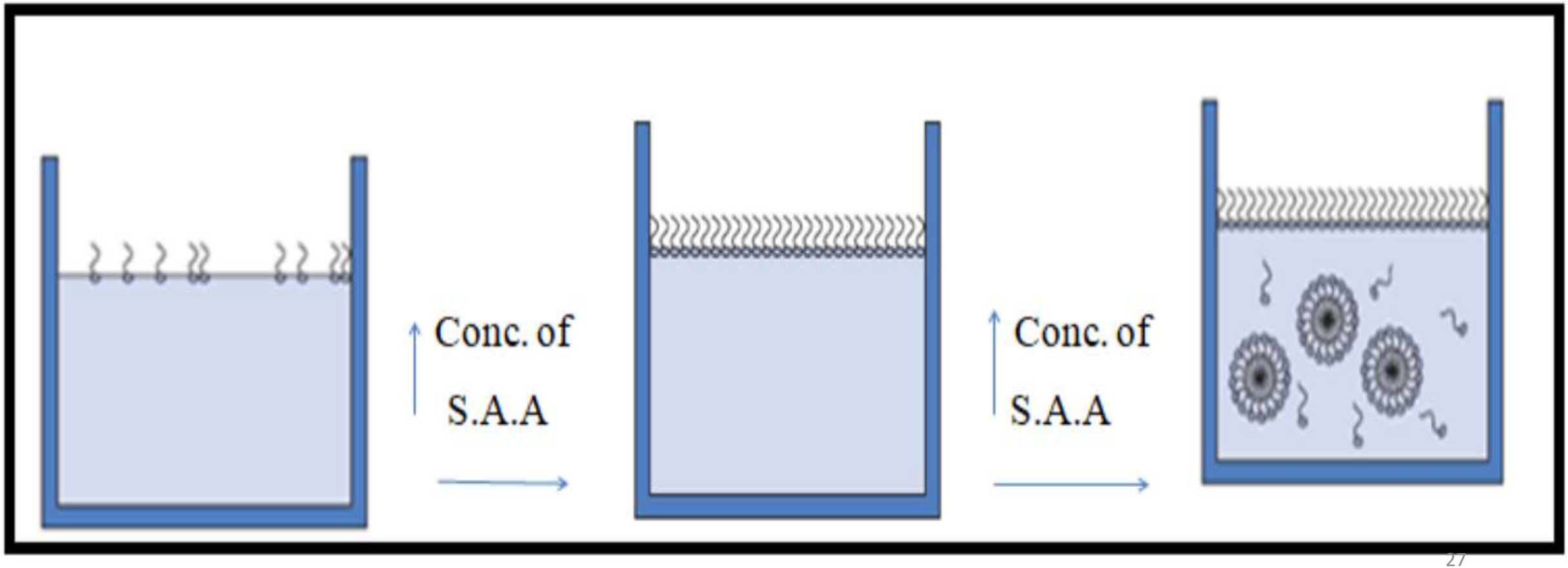
- The surface active agents **reduce surface tension** because when surfactant molecules adsorb at **the water surface**, the surfactant molecules **replace** some of the water molecules in the surface and the forces of attraction between surfactant and water molecules are **less** than those between two water molecules (interfere with hydrogen bond of water molecules), hence the contraction force is reduced.
- **The surface tension** decreases with **increasing concentrations of the surface active agent**; however, after a certain concentration of the surface active agent, the surface **tension stops decreasing** and reaches a plateau. This concentration is called **critical micelle concentration (CMC).**
- **(Note:-** materials that **concentrated in the bulk** of liquid **increase the surface tension** of a liquid and they are called surface **inactive** agents like (e.g., inorganic electrolytes such as NaCl and sugar**)**

- ***Why surface tension stops decreasing and reaches a plateau?***
  - This is because at this concentration the surface is **saturated** with surface active molecules and any increase in their concentration will cause them to form micelles in the bulk **.**
  - As more surface active agent is added to water, the surface of the water is covered by molecules of the surface active agent, and then **micelles start forming**



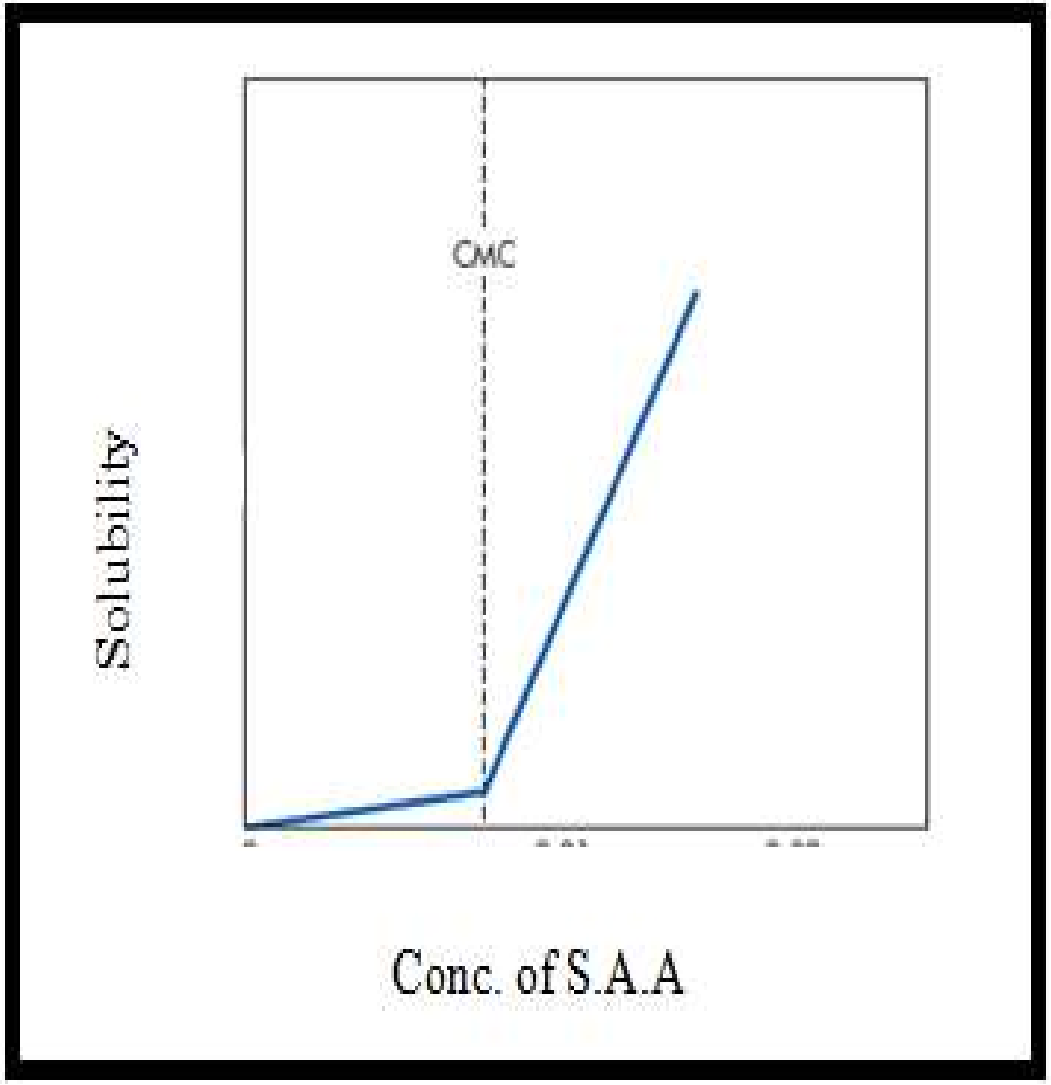


- ***Why micells are formed?***
  - To **protect their hydrophobic groups** from the aqueous environment



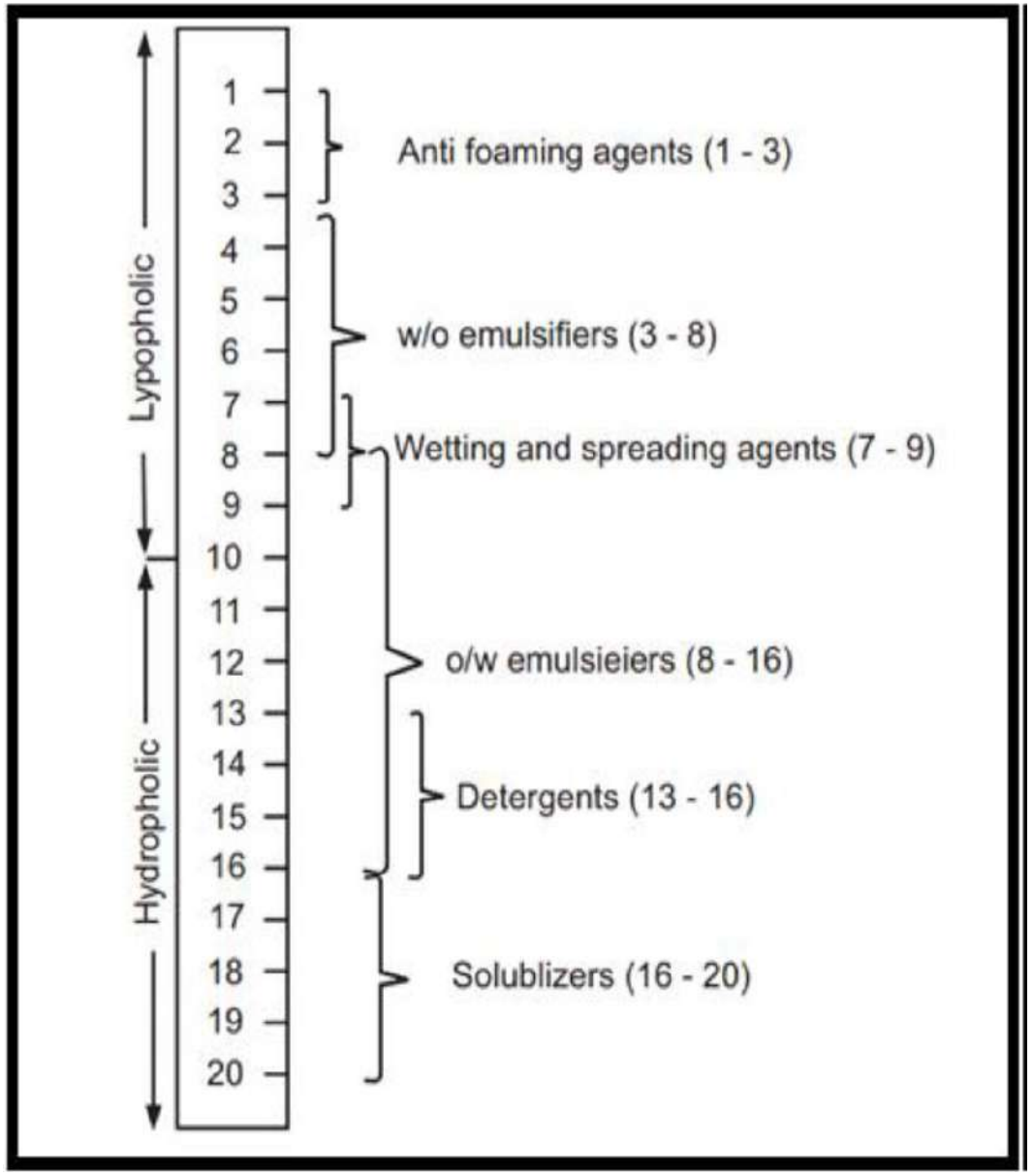
➢ *Effect of surfactant on solubility of slightly soluble substance*

- The ability of the solution to solubilize a drug, **increase sharply when the concentration of the surface active agent increases beyond the CMC concentration** since the nonpolar molecules in aqueous systems would be located in the hydrocarbon core of the micelle



Systems of Hydrophile–Lipophile Classification

- The hydrophile–lipophile balance (HLB) number is a measure of the balance between hydrophobic and hydrophilic portions of a surfactant.
- The HLB of a surfactant is expressed using an arbitrary scale which ranges from **0 to 20**
- At the **higher end** of the scale, the surfactants are hydrophilic and act as solubilising agents, detergents and oil-in-water emulsifiers.
- **Oil-soluble surfactants** have low HLB and act as water-in-oil emulsifiers.



A scale showing surfactant function on the basis of hydrophilic–lipophilic balance (HLB) values. Key: o/w = oil in water, w/o= water in oil


תודה
Dankie
Gracias
Спасибо
شكراً
Merci
Takk
Köszönjük
Terima kasih
Grazie
Dziękujemy
Dėkojame
Ďakujeme
Vielen Dank
Paldies
Täname teid
Kiitos
谢谢
Thank You
Tak
感謝您
Obrigado
Teşekkür Ederiz
감사합니다
Σας Ευχαριστούμ
ขอบคุณ
Bedankt
Děkujeme vám
ありがとうございます
Tack

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lec: 8
Interfacial Phenomena (part 2)

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Semester: 2nd

Adsorption at solid interfaces

- **Adsorption** of material at **solid interfaces** can take place from either an **adjacent liquid or gas phase**.
- The study of **adsorption of gases** arises in such diverse applications as the removal of objectionable odors from rooms and food, and the operation of gas masks.
- The principles of **solid–liquid adsorption** are used in decolorizing solutions, adsorption chromatography, detergency, and wetting.
- Thus, **adsorption** of this type can be considered as an attempt to reduce the surface free energy of the solid.
- **The surface tensions of solids** are **invariably more difficult to obtain** than those of liquids.
- In addition, **the solid interface** is **immobile in comparison to the turbulent liquid interface**.

The Solid–Gas Interface

- The **degree of adsorption** of **a gas by a solid** **depends** on :
  - the **chemical nature of the adsorbent** (the material used to adsorb the gas) and the **adsorbate** (the substance being adsorbed)
  - **the surface area of the adsorbent**
  - **the temperature**
  - **the partial pressure of the adsorbed gas.**
- **The types of adsorption** are generally recognized as **physical or van der Waals adsorption** and **chemical adsorption or chemisorption.**
- **Physical adsorption**, associated with van der Waals forces**, is reversible**, the removal of the adsorbate from the adsorbent being known as **desorption**.
  - A **physically adsorbed** gas can be desorbed from a solid by **increasing the temperature and reducing the pressure.**
- **Chemisorption**, in which the adsorbate is attached to the adsorbent by primary chemical bonds, is **irreversible unless the bonds are broken**.

The Solid–Liquid Interface

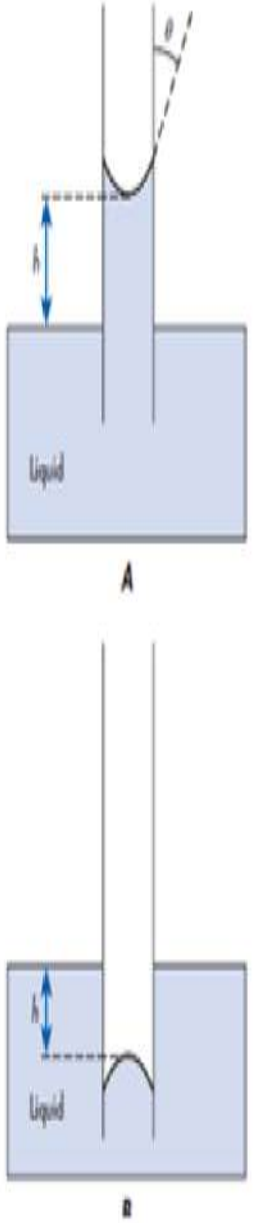
- Drugs such as dyes, alkaloids, fatty acids, and even inorganic acids and bases **can** be **adsorbed** from solution onto solids such as **charcoal and alumina**.
- The adsorption of solute molecules from solution can be treated in a manner **analogous** to the adsorption of molecules at the **solid–gas interface**.
- An **example** of a substance that can adsorb enormous amounts of gases or liquids is **activated charcoal**, the residue from destructive distillation of various organic materials, treated to increase its adsorptive power.
- To adsorb **more adsorbate**, an adsorbent of a given mass should have the **greatest possible surface area**. This might be achieved by the use of **porous or milled adsorbents**.
- **Activated charcoal** is made from material burnt in a superheated high-oxygen atmosphere, creating **small holes** in the range of 100 to 800 °A in diameter throughout the grain of the charcoal. This effectively increases the charcoal's surface area so that **the surface area of 1 g of charcoal is approximately 1000 m^2**.

Wetting phenomena and wetting agents

- **Wettability**: - is the property that indicate the **affinity** between **solid and fluid phase**
- **Talc or charcoal** sprinkled on the surface of water, they will float despite the fact that their densities are higher than that of water.
- In order for **wetting of solid to occur**, the liquid must **displace air** and **spread over the surface of the solid**, otherwise, we say that the solid is **NOT** wetted
- When a liquid comes into contact with the solid, the behavior of the liquid will depend on **the balance** between **the forces of attraction of molecules in the liquid (cohesion) and the forces of attraction between the liquid and the solid phases (adhesion)** .

Wetting phenomena and wetting agents

- In the case of **mercury and glass**, attractive forces between molecules of mercury and glass are much smaller than the forces of attraction between molecules of mercury themselves. As a result, mercury will come together as a single spherical drop.
- In contrast, for **water and glass**, attractive forces between the solid and liquid molecules are greater than the forces between molecules of liquid themselves, and so the liquid is able to wet the surface of the glass



A. Water can wet the glass

Because Adhesive forces more than cohesive

So water rise in side the capillary tube with concave surface

B .Mercury cannot wet the glass

Because cohesive forces more than adhesive

So mercury rise in side the capillary tube with convex surface

- Many pharmaceutical preparations require dispersion of solid in liquids
  - **Example**: The preparation of suspension requires that the fine solid particles immersed and then dispersed in a liquid vehicle, that is mean the **solid particles** have to be **wetted** in order to be dispersed in a liquid.
- The parameter that reflects the **degree of wetting** is known as **contact angle**
- **Contact angle (Θ):** - which is the angle between a liquid droplet and surface over which it spread . it range from 0-180° (Figure below)
  - **Θ = zero** means complete wetting (**glass** and **water**)
  - **Θ= 180°** means no wetting (water and greasy surface)
  - The contact angle may also have any **value between these limits (partial wetting**)

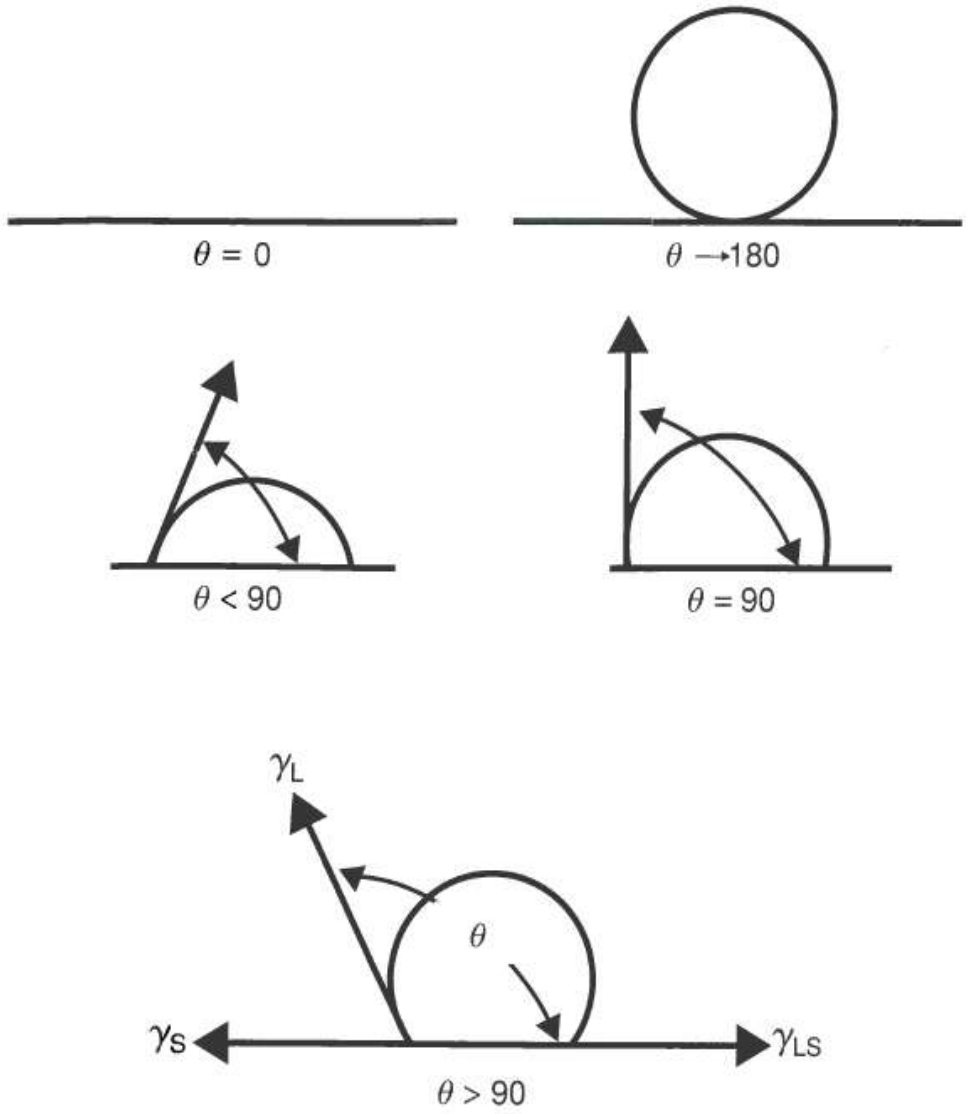


FIG. 15-24 Contact angles from 0° to 180°.

- **Hydrophilic materials** have **small contact angle** with water while hydrophobic material have large contact angle.
- **To increase wetting**, the contact angle should be **decreased** this is done by **adding surfactant** which is called **wetting agent**.
  - **A wetting agent** is a **surfactant** that, when dissolved in water, **lowers the contact angle**, aids in displacing an air phase at the surface, and replaces it with a liquid phase.
- **Examples of the application of wetting to pharmacy and medicine:**
  - **The displacement of air** from the surface of **sulfur, charcoal**, and other powders for the purpose of dispersing these drugs in liquid vehicles
  - **The displacement of dirt** by the **use of detergents** in the washing of wounds; and the application of medicinal lotions and sprays to the surface of the skin and mucous membranes

Applications of surface-active agents

1. **As emulsifying** agents by **decrease Interfacial tension**
2. **Wetting agents** by **decreasing the contact angle;** wetting is the first step for dispersing a solid in a liquid vehicle
3. **Detergents**; which are surfactants that are used for **removal of dirt**
4. **Solubilizing agents** by formation of **micells**
5. A surfactant **may** affect the **activity of a drug**.
   - The presence of a **low concentration** of **surfactant** will **potentiate** **the activity of anthelmintic drug.**
   - This potentiation of activity is due to a **reduction in interfacial tension** between the **liquid phase and the cell wall of the organism.**
   - As a result, the **adsorption** and **spreading** of the drug over the surface of the organism is facilitated.
   - When the **concentration** of surface-active agent present **exceeds** that required amount it will form **micelles** and the **rate of penetration** of the anthelmintic **decreases** nearly to **zero**.
   - This is because the drug is now partitioned between the micelles and the aqueous phase, resulting in a reduction in the effective concentration. or may itself exert drug action

Applications of surface-active agents

6. A surfactant **may exert a drug action**

- **Quaternary ammonium compounds** are examples of surface-active agents that in themselves possess **antibacterial activity.**
- This may **depend in part on interfacial phenomena**, but other factors are also important.
  - The agents are **adsorbed** on the cell surface and supposedly **bring about destruction by increasing the permeability** or "leakiness" of the lipid cell membrane.
  - **Death** then occurs through **a loss of essential materials** from the cell.
- Both **gram-negative and gram-positive** organisms are susceptible to the action of the **cationic quaternary compounds**

Foam and antifoaming agents

- Any solutions containing surface-active materials produce **stable foams when mixed intimately with air**.
- A **foam** is a relatively **stable structure consisting of air pockets enclosed within thin films of liquid**, the gas-in-liquid dispersion being stabilized by a **foaming agent**.
- The foam dissipates as the liquid drains away from the area surrounding the air globules, and the film finally collapses.
- Agents such as **alcohol, ether, castor oil, and some surfactants** can be used to **break the foam** and are known as **antifoaming agents**.
- Foams are **sometimes** useful in pharmacy (e.g., antimicrobial formulations) but are usually a nuisance and are prevented or destroyed when possible.
- **The undesirable foaming** of solubilized liquid preparations **poses a problem in formulation**.

Electrical Properties of interfaces

Electric Properties - charge on the surface of a particle

- Particles dispersed in liquid media may become charged mainly in one of two ways.
- The first involves the **selective adsorption of a particular ionic species present in solution.**
  - This may be an **ion added** to the solution or, in the *case of* ***pure water****, it may be the* ***hydronium or hydroxyl ion.***
  - **The majority** of particles dispersed in water acquire a **negative charge** due to preferential adsorption of the **hydroxyl ion** because the hydronium ion is more hydrated than hydroxyl ion , so they have greater tendency to be in the bulk of aqueous medium , whereas the less **hydrated hydroxyl** ion have greater tendency to be **adsorbed at the surface of particle**
- Second, **charges on particles arise from ionization of groups that may be situated at the surface of the particle**. In these cases, the **charge** is a function of **pH and pKa .**
  - Example amino acid and protein (have COOH and NH_2) groups on their structure
    - **At low pH** , the protein will **have +ve charge due to ionization of -NH_2 groups to –$NH3^+$**
    - **At high pH** the protein will **have –ve charge due to ionization of –COOH groups to –COO^-**
    - **At certain pH** (specific for each protein), the **total no. of +ve charge equal to the total no. of –ve charge and the net charge will be zero**
      - This pH is termed as **isoelectric point** of protein and the protein exists as **Zwitterion**

The Electric Double Layer

- Consider a solid surface in contact with a **polar solution containing ions**, for example, an aqueous solution of an **electrolyte**.
- Furthermore, let us suppose that **some of the cations are adsorbed onto the surface**, giving it a **positive charge.**
- Remaining in solution are the **rest** of the cations plus the **total** number of **anions** added.
- These **anions** are **attracted to the positively charged surface by electric forces** that also serve to **repel** the approach of any further **cations** once the initial adsorption is complete.
- **In addition** to these **electric forces**, **thermal motion** tends to produce an **equal distribution of all the ions in solution.**
- As a result, an **equilibrium situation is set up in which some of the excess anions approach the surface, whereas the remainders are distributed in decreasing amounts as one proceeds away from the charged surface.**
- **At a particular distance from the surface**, the concentrations of anions and cations are equal, that is, conditions of **electric neutrality prevail.**
- It is important to remember that the **system** as a **whole** is **electrically neutral**, even though there are **regions of unequal distribution of anions and cations**.
- Such a situation is shown in the Figure 1, where aa’ is the surface of the solid.

- **The adsorbed ions** that give the **surface** its **positive charge** are referred to as **the potential-determining ions**.
- Immediately adjacent to this surface layer is a region of tightly bound solvent molecules, together with some **negative ions**, also tightly bound to the surface. The limit of this region is given by the **line bb**′ in the Figure
- **These ions**, having a **charge opposite** to that of **the potential-determining ions**, are known as **counterions or gegenions**.
- The degree of attraction of the solvent molecules and counterions is such that if the surface is moved relative to the liquid, the shear plane is bb′ rather than aa′, the true surface.
- In **the region** bounded by the **lines bb′ and cc′,** there is an **excess of negative ions**. The **potential at bb′ is still positive** because, as previously mentioned, there are fewer anions in the **tightly bound layer** than cations adsorbed onto the surface of the solid.
- Beyond **cc′**, **the distribution of ions is uniform and electric neutrality is obtained.**
- Thus, **the electric distribution at the interface** is **equivalent to a double layer of charge**, the first layer (extending from aa′ to bb′) tightly bound and a second layer (from bb′ to cc′) that is more diffuse. The so-called diffuse double layer therefore extends from aa′ to cc′.

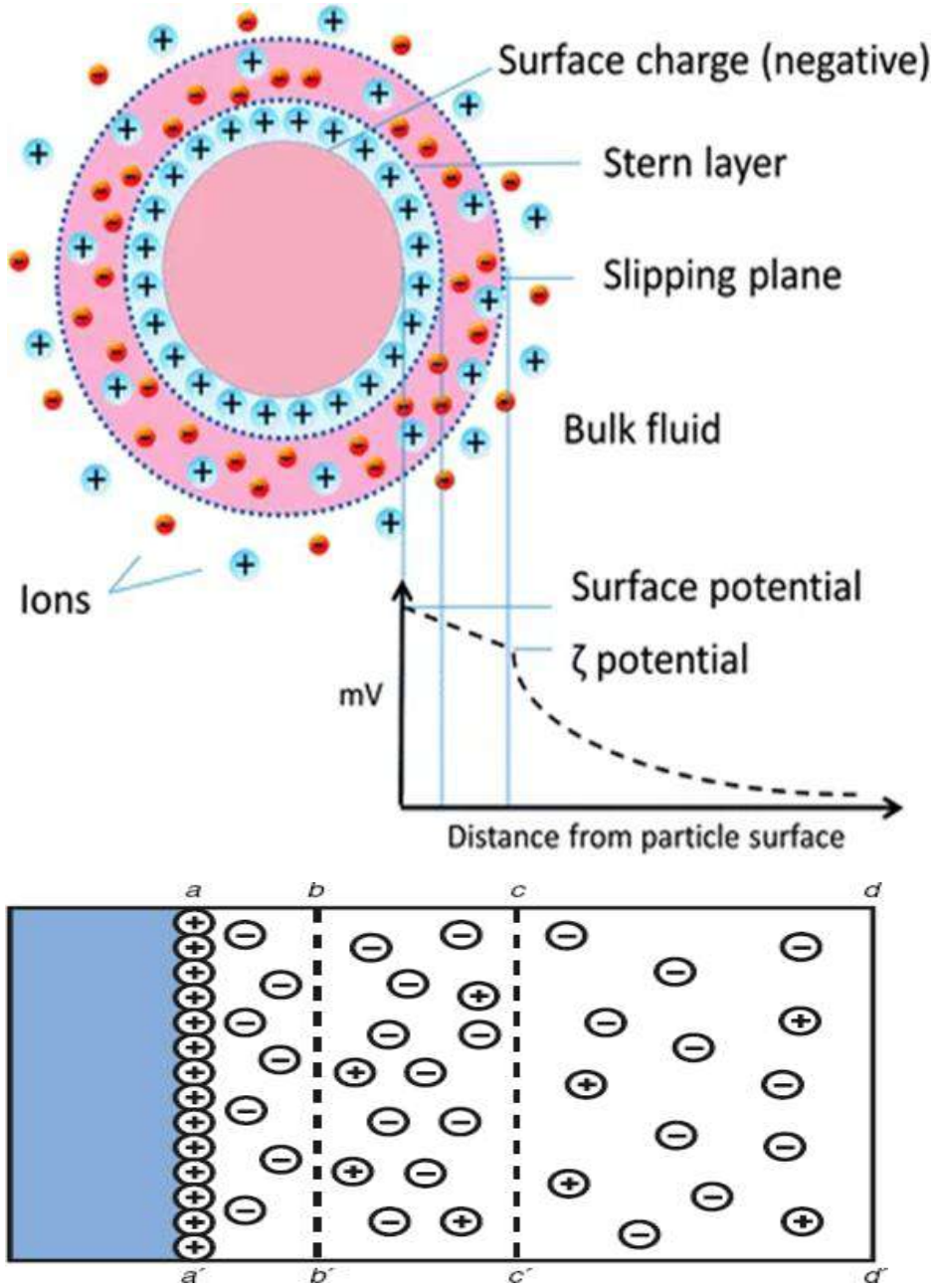
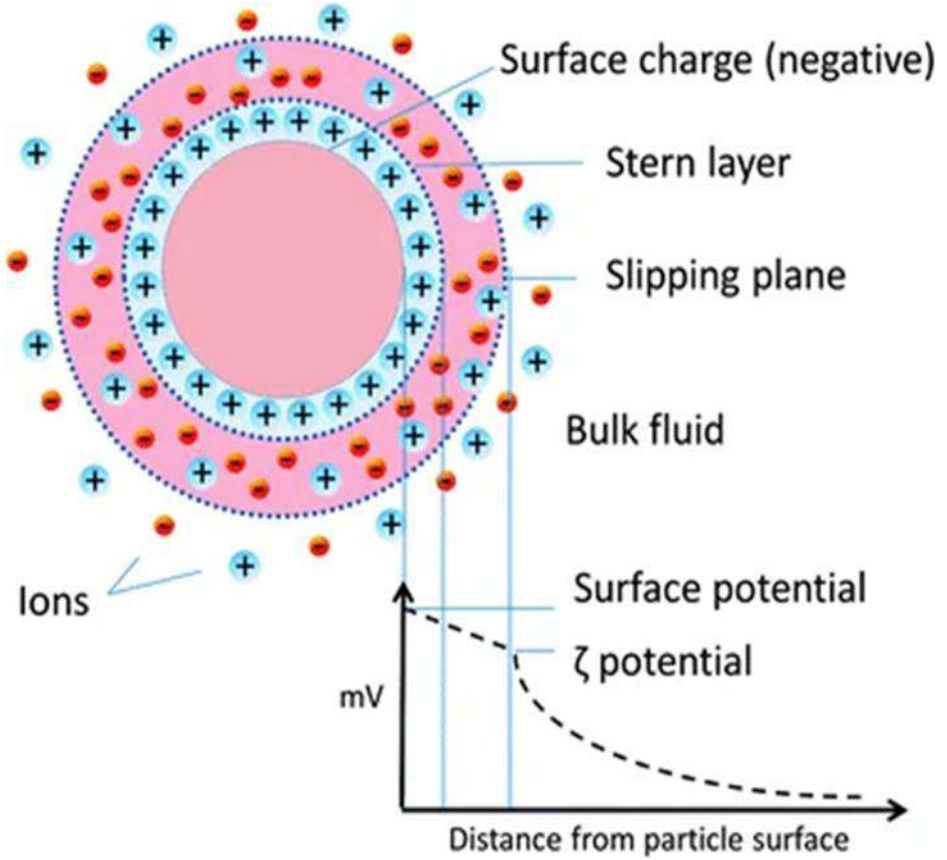
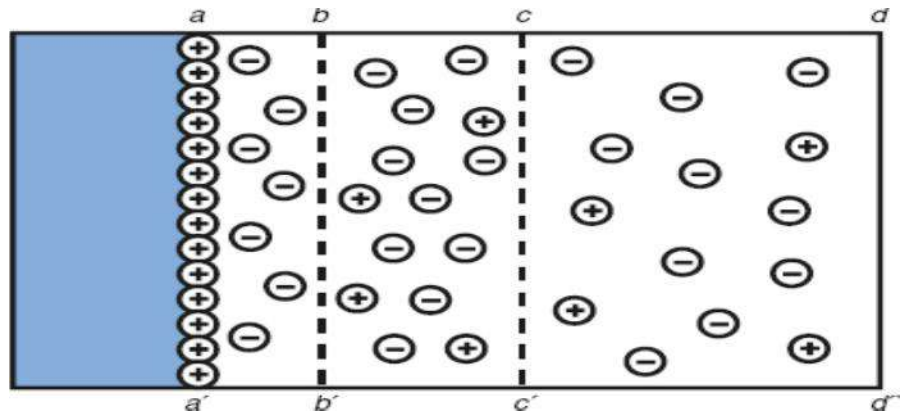


FIG. The electric double layer at the surface of separation between two phases, showing distribution of ions. The system as a whole is electrically neutral.

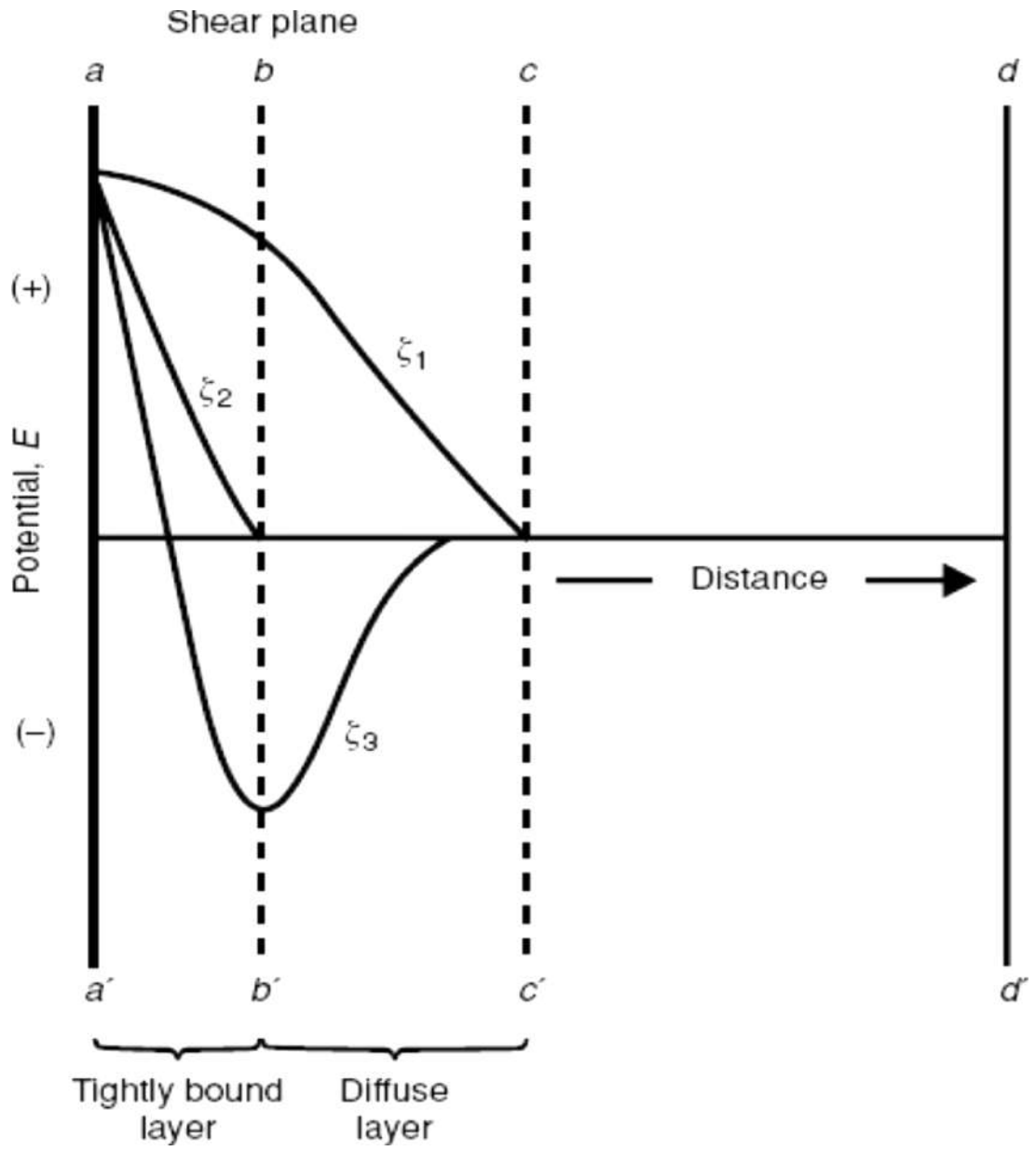
- Two situations other than that represented by the figure are possible:
  a. If the **counterions** in the tightly bound, solvated layer equal the positive charge on the solid surface, then electric **neutrality** occurs **at the plane bb′** rather than cc′.
  b. Should the total charge of the **counterions** in the region **aa′–bb′ exceed** the charge due to the potential-determining ions, then the **net charge at bb′ will be negative rather than less positive**.
  - This means that, in this instance, for electric **neutrality to be obtained at cc′,** an excess of **positive ions** must be present in the region **bb′–cc′.**
  - The student should appreciate that if the potential-determining ion is **negative**, the arguments just given still apply, although now positive ions will be present in the tightly bound layer.





Nernst and Zeta Potentials

- The changes in potential with distance from the surface for the various situations discussed in the previous section can be represented as shown in Figure 15-29.
- **The potential** at the solid surface aa′ due to the potential-determining ion is **the electrothermodynamic *(Nernst) potential, E,*** and is defined as **the difference in potential between the actual surface and the ectroneutral region of the solution.**
- **The potential** located at the **shear plane bb'** is known as the **electrokinetic, or zeta, potential**, ***The zeta potential, ζ is defined as the difference in potential between the surface of the tightly bound layer (shear plane) and the electroneutral region of the solution.***
- As shown in Figure 2, the potential initially drops off rapidly, followed by a more gradual decrease as the distance from the surface increases. This is because the counterions close to the surface act as a screen that reduces the electrostatic attraction between the charged surface and those counterions further away from the surface.



Nernst and Zeta Potentials

- **The zeta potential** has practical application in the stability of systems containing dispersed particles because this potential, rather than the Nernst potential, it governs the degree of repulsion between adjacent, similarly charged, dispersed particles.
- **If the zeta potential** is reduced below a certain value (which depends on the particular system being used), the attractive forces exceed the repulsive forces, and the particles come together. This phenomenon is known as **flocculation**.

Effect of Electrolytes

- As the **concentration of electrolyte** present in the system is increased, the **potential falls off more rapidly** with **distance** and the **thickness** of the **double layer decreased**.
- A similar situation occurs when **the valency of the counterion is increased** while the **total concentration** of electrolyte is held **constant**. The overall effect frequently causes **a reduction in zeta potential**.

Application of Zeta potential

1- Interfacial Properties of Suspended Particles

- The particles in a liquid suspension tend to ***flocculate***, that is, to form light, fluffy conglomerates that are held together by weak van der Waals forces, but under certain conditions, the particles **may** adhere by stronger forces to **form** what are termed ***aggregates or cake***
- When the repulsion energy (**zeta potential**) is high, the **collision** of the particles is **opposed**.
- The system remains ***deflocculated*** (dispersed or suspended), and, when sedimentation is complete, the particles form a close-packed arrangement with the smaller particles filling the voids between the larger ones.
- Those particles **lowest** in the **sediment** are gradually pressed together by the weight of the ones above and they will adhere together by strong **forces** to form ***aggregares or cake***. To re-suspend and re-disperse these particles, it is again necessary to overcome these forces. Because this is not easily achieved by **agitation**, the particles tend to **remain strongly attracted** to each other and **form a hard cake**.
- ***Flocculated particles*** are weakly bonded, settle rapidly, do not form a cake, and are easily re-suspended.
- Therefore, a very high +ve or –ve zeta potential is not preferred in preparation of suspension, but **its value should be controlled within certain limit** as shown in the figure below, and this is done by **adding a flocculating agents**

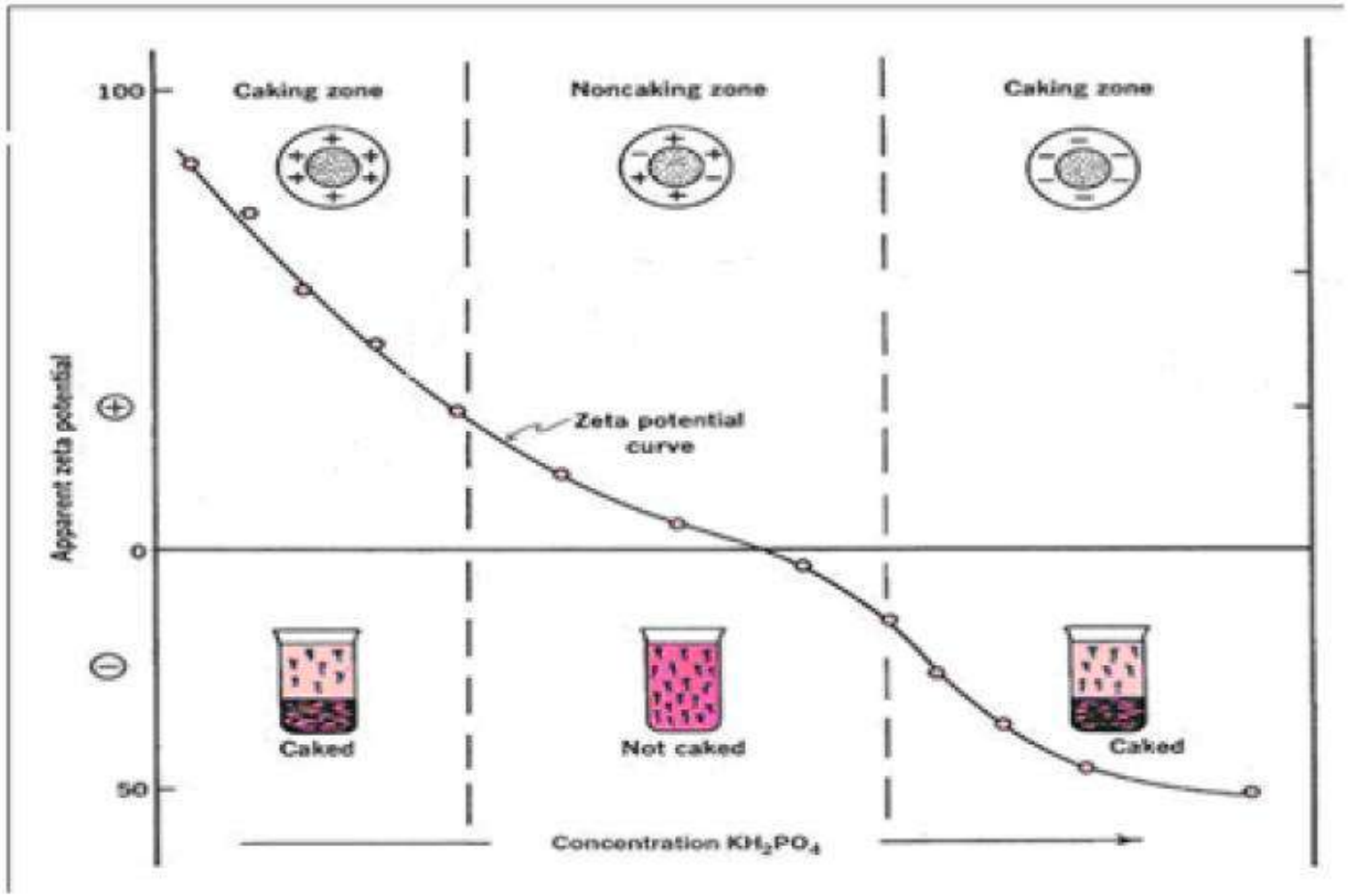


Fig. 3. Caking diagram, showing the flocculation of suspension by means of the flocculating agent monobasic potassium phosphate

Application of Zeta potential

2- Electrokinetic Phenomena

- These are effects that occur when **charged particles** or surfaces interact with a liquid under motion or an electric field.
- Example: movement of a charged surface relative to a liquid.T
- he most important application here is **electrophoresis**.

3- Electrophoresis:

- Involves **the movement of a charged particle through a liquid under the influence of an applied potential difference.**
- **An electrophoresis cell** fitted with two electrodes contains the dispersion.
- When a **potential is applied** across the electrodes, the particles migrate to the oppositely charged electrode.
- From knowledge of the direction and rate of migration , the sign and magnitude of **zeta potential can be determined.**
  - **Direction of movement → tells you the sign of the charge**
  - **Speed of movement → relates to the magnitude of zeta potential**
- It is mainly used for **separation of plasma protein**.