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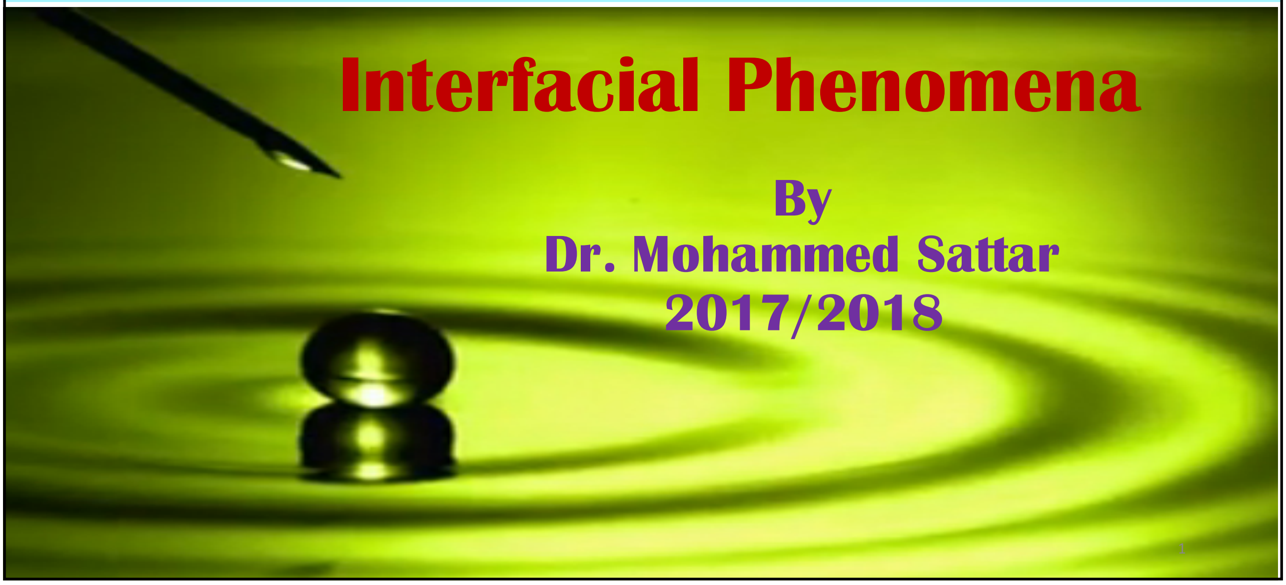


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# Objectives

- Differentiation bt interfacial and surface tension
- Method of measurements of surface tension
- Spreading coefficient
- Surface adsorption
- SAA and their Classification
- Wetting agent

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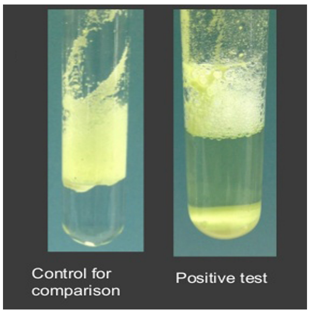
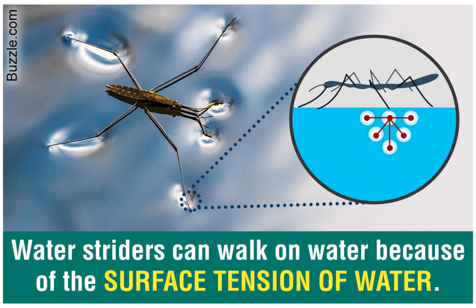
# Applications




**Clinical test for jaundice:** Normal urine has a surface tension of about 66 dynes/centimeter but if bile is present (a test for jaundice), it drops to about 55. In the Hay test, powdered sulfur is sprinkled on the urine surface. It will float on normal urine, but will sink if the surface tension is lowered by the bile.

**Walking on water:** The water strider can walk on water because their weight is not enough to penetrate the surface.




**Floating a needle:** A carefully placed small needle can be made to float on the surface of water even though it is several times as dense as water. If the surface is agitated to break up the surface tension, then needle will quickly sink.

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# Applications

**Soaps and detergents**: These help the cleaning of clothes by lowering the surface tension of the water so that it more readily soaks into pores and soiled areas.

**Washing with cold water:** The major reason for using hot water for washing is that its surface tension is lower and it is a better wetting agent. But if the detergent lowers the surface tension, the heating may be unnecessary.

**Don't touch the tent!:** Common tent materials are somewhat rainproof in that the surface tension of water will bridge the pores in the finely woven material. But if you touch the tent material with your finger, you break the surface tension and the rain will drip through.

- **Surface tension disinfectants:** Disinfectants are usually solutions of low surface tension. This allow them to spread out on the cell walls of bacteria and disrupt them.

**Why bubbles are round:** The surface tension of water provides the necessary wall tension for the formation of bubbles with water. The tendency to minimize that wall tension pulls the bubbles into spherical shapes.

**Surface Tension and Droplets:** Surface tension is responsible for the shape of liquid droplets. Although easily deformed, droplets of water tend to be pulled into a spherical shape by the cohesive forces of the surface layer.

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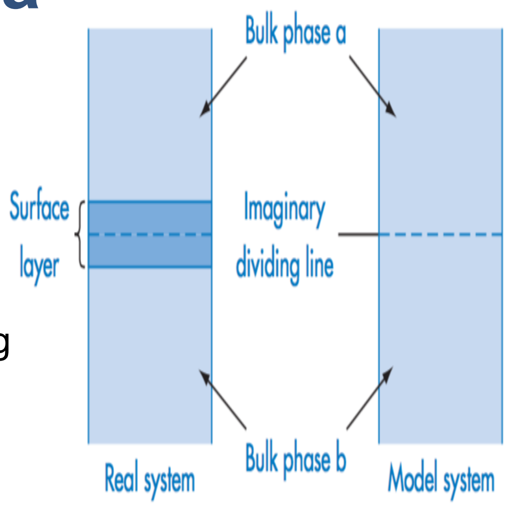
# Interfacial Phenomena

- A common boundary bet 2 phases is termed an interface.

- The properties of the molecules forming the interface are often sufficiently differ from both of those in the bulk of other 2 phases that they are referred to as forming an **interfacial phase.**

- Molecules in the Interfacial phase are in a **dynamic motion**

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# Interfacial Classification

- Several types of interface can exist, depending on the nature of the adjacent phases (e.g.: solid, liquid or gaseous state).

1) *liquid interfaces* (G-L, L-L)
2) *solid interfaces.* (L-S, S-S)

- Note: The term **surface** is used for the description of G-S or G-L interface.

"**Every surface is an interface**"

# Interfacial Classification

| Phase | Interfacial Tension | Types & Examples of Interface |
|---|---|---|
| G-G | - | **No interface possible** |
| G-L | $\gamma_{LV}$ | **Water exposed to atmosphere** |
| G-S | $\gamma_{SV}$ | **Table top** |
| L-L | $\gamma_{LL}$ | **Emulsion** |
| L-S | $\gamma_{LS}$ | **Suspension** |
| S-S | $\gamma_{SS}$ | **Powder particles in contact** |



# Pharmaceutical Importance of Interfacial Phenomena

a. Adsorption of drugs onto the surroundings.

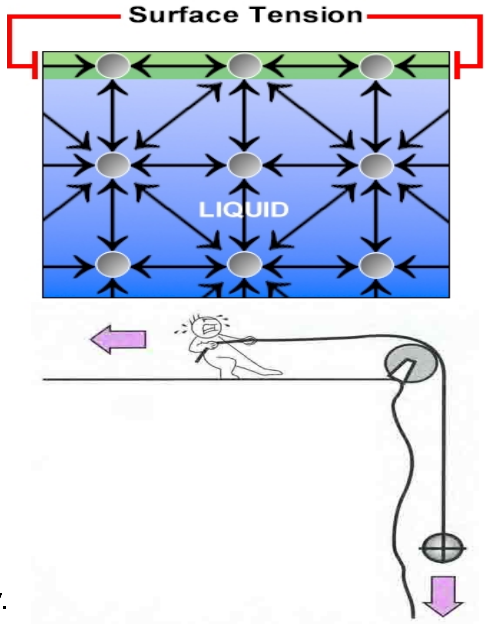
b. Penetration of molecules through biological membranes.

c. Emulsion and suspension formation and stability.

d. Respiration (SAA in alveoli).

# Liquid Interfaces

- Molecules at the surface are not completely surrounded by other molecules.
- Inward attraction of the molecules on the surface lead to surface contraction ( called ………).
- The contraction of the surface is spontaneous; that is, it is accompanied by ……… in free energy.
- The contracted surface thus represents a minimum free energy state and any attempt to expand the surface must involve an increase in the free energy.

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# Liquid Interfaces

- **Surface tension (ɣ)**: a force/ length that must be applied parallel to the surface to counteract the net inward pulling.
- A similar imbalance of attractive forces exists at the interface between two immiscible liquids.
- **Interfacial tension** : a force/ length bet 2 immiscible phases.
- The interfacial tension at the octanol-water interface is considerably lower than the surface tension of octanol owing to hydrogen bonding between these two liquids.
- Units: **dynes/cm** or **mN/m**

**Table 6.1** Surface tensions of pure liquids and interfacial tensions against water at 20°C

| Substance | Surface tension ($mN\ m^{-1}$) | Interfacial tension ($mN\ m^{-1}$) |
|---|---|---|
| Water | 72 | — |
| Glycerol | 63 | — |
| Oleic acid | 33 | 16 |
| Benzene | 29 | 35 |
| Chloroform | 27 | 33 |
| *n*-Octanol | 27 | 8.5 |
| Carbon tetrachloride | 27 | 45 |
| Castor oil | 39 | — |
| Olive oil | 36 | 33 |
| Cottonseed oil | 35 | — |
| *n*-Octane | 22 | 51 |
| Ethyl ether | 17 | 11 |

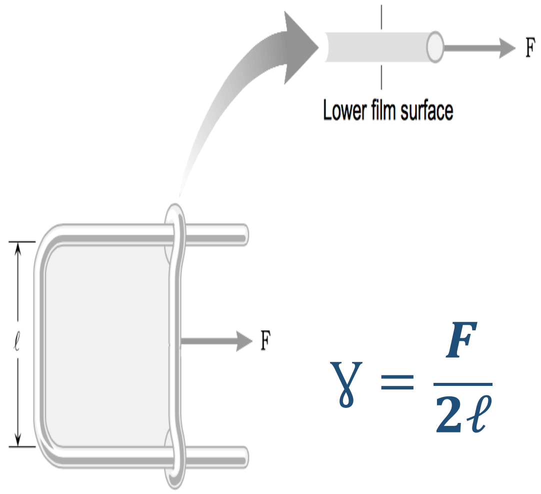


- $\gamma$ of most liquids ↓ almost linearly with an ↑ in temperature, that is, with an ↑ in the kinetic energy of the molecules.
- In the region of its critical temperature, the surface tension of a liquid becomes zero.
- The surface tension of water at
  a) 0°C it is 75.6
  b) 20°C it is 72.8,
  c) 75°C it is 63.5 dynes/cm.

# Liquid Interfaces

- S.T. is best explained by formation of **films** and **bubbles**.

- S.T. is demonstrated by 3-Frame wire connected w movable bar, when immersed in soap solution, film would be formed. The force required to move the bar until the film break represent the S.T.




$$\gamma = \frac{F}{2\ell}$$



# Surface Free energy

- Molecules on the surface have higher potential energy than the rest of the molecules in the bulk.
- The larger the surface , more molecules have higher energy.
- Liquid droplet has a spherical shape, why?
- ↑ in energy of the liquid lead to ↑ the surface of the liquid.
- Work (W) must be done to increase liquid surface.

$$W = \gamma \Delta A$$

- Where W is work done or surface free energy increase express in ergs(dyne cm); $\gamma$ is surface tension in dynes/cm and $\Delta A$ is increase in area in $cm^2$.

## *Measurement of Surface and Interfacial Tensions*

1) Capillary Rise Method.
2) The DuNoüy Ring Method
3) Drop weight method (Stalagmometer) ,
4) Bubble pressure,
5) Wilhelmy plate,

**The choice of the method for measuring surface and interfacial tension depend on:**

- **Whether surface or interfacial tension is to be determined.**
- **The desired accuracy**
- **The size of sample.**

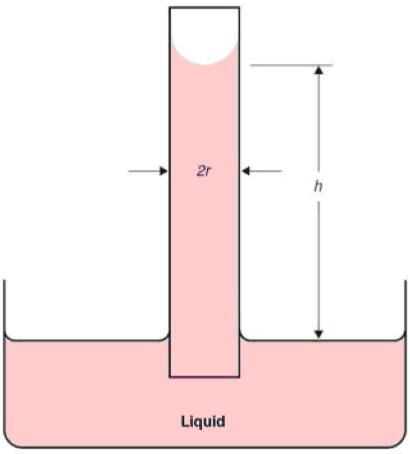


## Capillary Rise Method

- Capillary tube is immersed in a liquid contained in a beaker, the liquid would rise up the tube a certain distance.
- It is used for S.T. but not to $\gamma_{LL}$, and $\gamma_{LS}$.

$$\gamma = \frac{1}{2} rhpg$$

- Where r (radius, cm), h (height, cm), p (density, g/cm$^2$), g (acceleration of gravity, 980 cm/sec$^2$)



# The DuNoüy Ring Method

- The *DuNoüy tensiometer* is widely used for measuring surface and interfacial tensions.

- The force necessary to detach a platinum–iridium ring immersed at the surface or interface is proportional to the surface or interfacial tension.

- 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.

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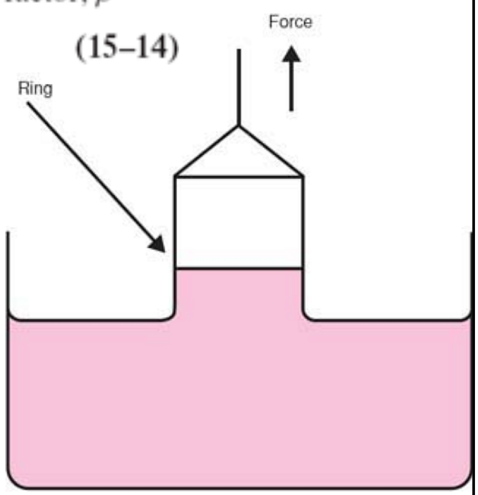
$$\gamma = \frac{\text{Dial reading in dynes}}{2 \times \text{Ring circumference}} \times \text{Correction factor, } \beta \quad (15\text{–}14)$$

➢A correction factor depends on:

1) Radius of the ring,
2) Radius of the wire used to form the ring,
3) Volume of liquid raised out of the surface.

➢Errors as large as 25% may occur if the correction factor is not calculated and applied.



# Spreading Coefficient

- Adhesion force is ………… .
- Cohesion force is ………… .
- Oleic acid is placed on the surface of water, it will spread as a film if:

Adhesion oleic-water > Cohesion of oleic-oleic.

- The term *film* used here applies to a *duplex film, bec …….*
- Duplex films (100 Å or more).

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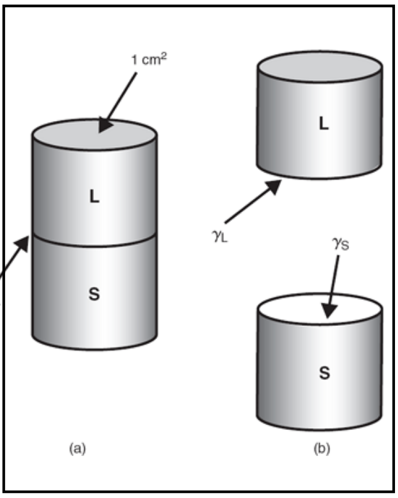
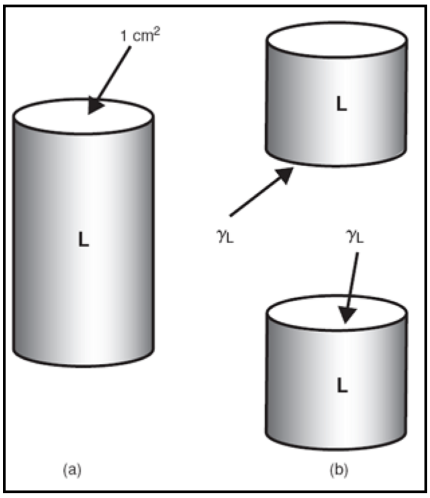
# Spreading Coefficient

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## Spreading Coefficient

- The *work of adhesion ($W_a$)*, is the energy required to break the attraction between the unlike molecules.

$$W_a = \gamma_L + \gamma_S - \gamma_{LS}$$

- The *work of cohesion ($W_c$)*, required to separate the molecules of the spreading liquid so that it can flow over the sublayer,

$$W_c = 2\gamma_L$$

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## Spreading Coefficient

- *Spreading coefficient (S)* = ($W_a$ - $W_c$)

- if it is positive, the oil will spread over a water surface.

$$S = W_a - W_c = (\gamma_L + \gamma_S - \gamma_{LS}) - 2\gamma_L$$

$$S = \gamma_S - (\gamma_L + \gamma_{LS})$$

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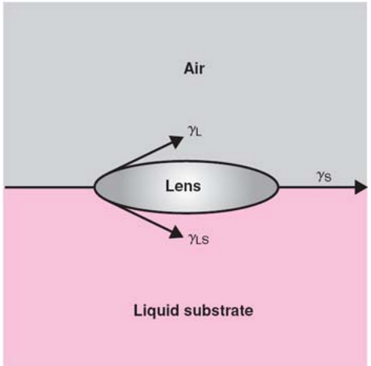
# Spreading Coefficient

- Spreading occurs (*S* is positive) when the surface tension of the sublayer liquid ($\gamma_S$) is greater than the sum of the surface tension of the spreading liquid and the interfacial tension between the sublayer and the spreading liquid ($\gamma_L + \gamma_{LS}$).

- If ($\gamma_L + \gamma_{LS}$) is larger than $\gamma_S$, the substance forms globules or a floating lens and fails to spread over the surface. An example of such a case is mineral oil on water.

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# Spreading Coefficient

- Effects of Molecular Structure on (**S**)
  - a. **Polar groups** such as COOH or OH (propionic acid and ethanol) have high values of S.
  - b. Increase in carbon chains of acids will lead to **decrease of polar-nonpolar ratio** thus decrease in **S** on water (nonpolar liquid petrolatum fail to spread on water).
- Organic liquids on water are unstable, e.g. benzene
- Does benzene (Ex HW p. 363) spread in water because of polarity ?

## Pharmaceutical applications of S

- The surface of the skin is bathed in an aqueous–oily layer having a polar–nonpolar character similar to that of a mixture of fatty acids.

- For a lotion with a mineral oil base to spread freely and evenly on the skin, its polarity and hence its spreading coefficient should be increased by the addition of a surfactant.

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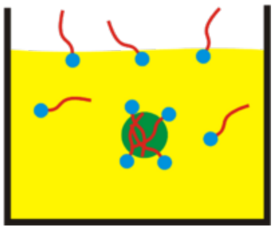
# Adsorption at Liquid Interfaces

➢Positive adsorption : Molecules and ions adsorbed (such as ……) at interface leading to:

$\downarrow \gamma$ and $\downarrow$**W**

➢Negative adsorption: Inorganic electrolytes favor partitioned in the bulk and lead to: .

$\uparrow \gamma$ and $\uparrow$**W**



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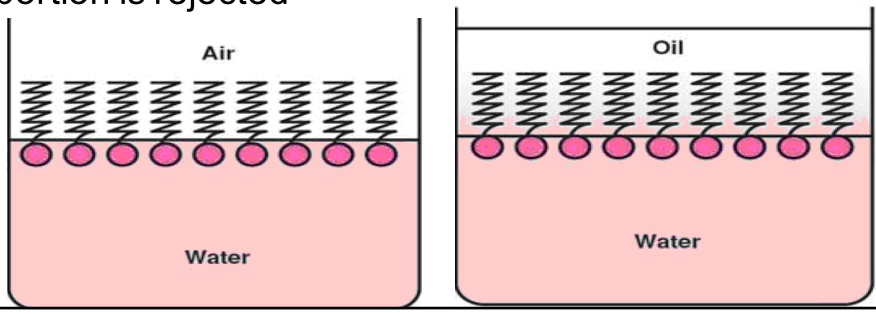
# Surface active agent “Surfactant”

- Subs adsorb at the surface and lower surface and interfacial tension
- They are amphiphilic molecules have a balanced hydrophilic – lipophilic properties.
- The polar group is able to associate with the water molecules. The nonpolar portion is rejected



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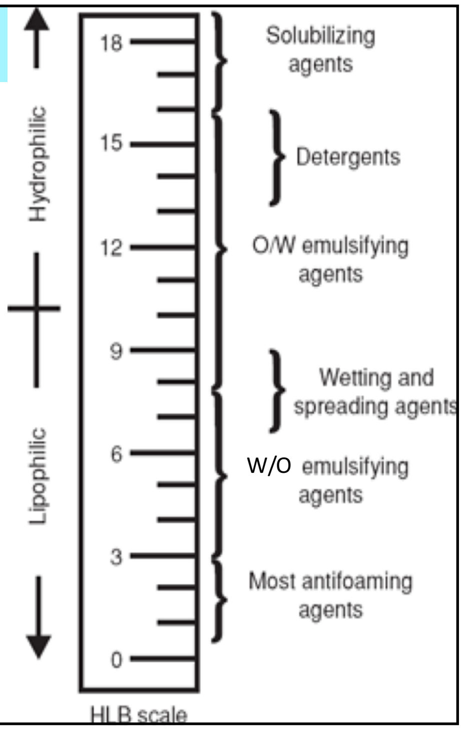
# Systems of H–L Classification

- The higher the HLB of an agent, the more hydrophilic it is.
- The Spans, sorbitan esters , are lipophilic and have low HLB values (1.8–8.6);
- The Tweens, polyoxyethylene derivatives of the Spans, are hydrophilic and have high HLB values (9.6–16.7).



# Examples of SAA

- Non ionic SAA: Tweens and spans
- Cationic SAA: Quaternary ammonium compounds.
- Anionic SAA: Fatty acid salt (soap, sod oleate)

- Example 15-8: Required HLB , home work.



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# Micelles

➢When present in a liquid medium at low concentrations, the amphiphiles exist separately.

➢As the concentration is increased, aggregation occurs. These aggregates, which may contain 50 or more monomers, are called *micelles*

➢The concentration of monomer at which micelles form is termed the *critical micelle concentration*(*CMC*).

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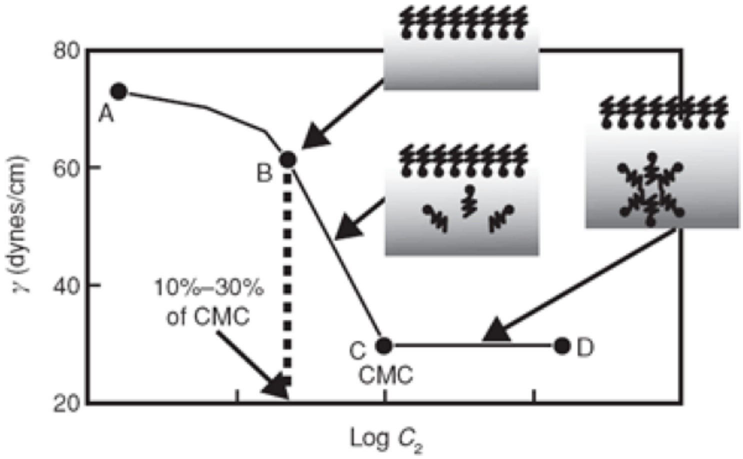


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# Adsorption at Solid Interfaces

**A. solid–gas adsorption:**

- Removal of objectionable odors from rooms and food,
- Gas masks,
- the measurement of the dimensions of particles in a powder.

**B. solid–liquid adsorption:**

- decolorizing solutions,
- adsorption chromatography,
- detergency, wetting.

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# The Solid–Liquid Interface

- Drugs such as dyes, alkaloids, fatty acids, and inorganic acids and bases can be absorbed from solution onto solids such as **charcoal** and **alumina**.
- Activated charcoal : reduced p.s. by milling and increased SA of adsorption, used as anti-dote for sulfonylureas, phenobarbital and acetaminophen
- Diphtheria toxins adsorbed on clay.
- Quinidine sulfate absorption decreased by anti-diarrheal preparation (Bismuth and Mg trisilicate)
- Antibiotic adsorbed on sucrose or sorbitol when blending.

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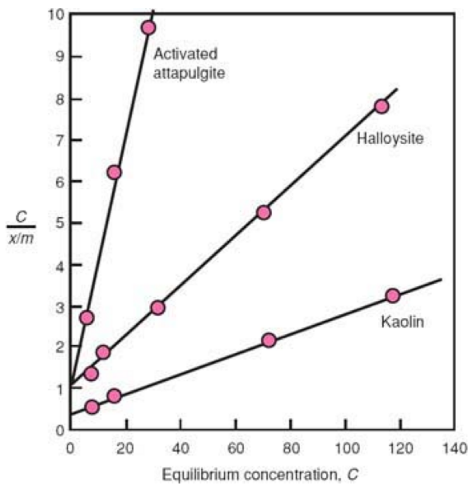
Adsorption of strychnine on various clays



# Wetting

- Type of SAA that reduce contact angle of liquids.
- Adsorption at solid surfaces : wetting and detergency.
- Attraction bet L-S is stronger than L-G.
- Behavior of liquid depends on attraction of L-L and attraction of L-S.

1) Mercury and glass:

**Mer-Glass < Mer-Mer.**

- As a result, mercury will come together as a single spherical drop.

2) Water and glass:

**Water-Glass > Water-water**

- so the water is able to wet the surface of the glass.

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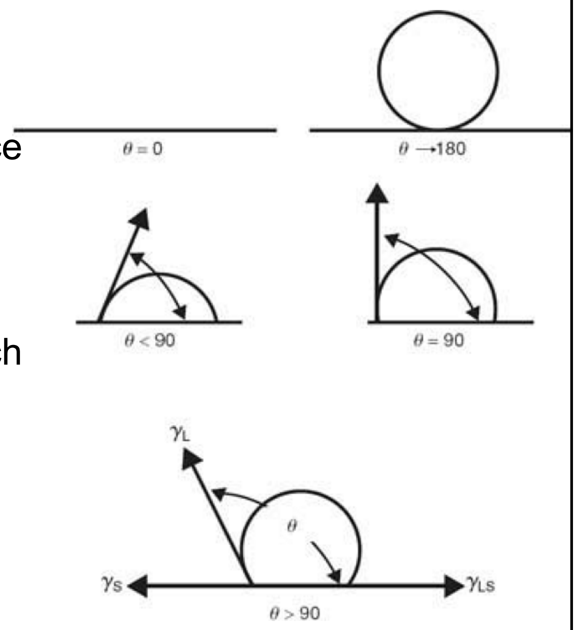
# Wetting

➢The contact angle (***θ***) is the angle between a liquid droplet and the surface over which it spreads.

➢the contact angle between a liquid and a solid may be 0° signifying complete wetting, or may approach 180°, at which wetting is insignificant.

➢Wetting agent reduce ***θ*** by displacing an air phase at the surface, and replaces it with a liquid phase.



## *Pharmaceutical applications of wetting*

1. Dispersing of molecules (such as sulfur, and charcoal) in water
2. Application of medicinal lotions and sprays to the surface of the skin and mucous membranes.
3. Wetting of tablet surfaces influences disintegration and dissolution.

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## *Pharmaceutical applications of SAA*

1. Surfactant
2. Emulsifying agent
3. Wetting agent
4. Solubilizing agent
5. Detergent
6. Antibacterial action
7. Absorption enhancers
8. Foaming agent
9. Antifoaming agent
10. Lung SAA protect alveoli

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# Thanks for your attention

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