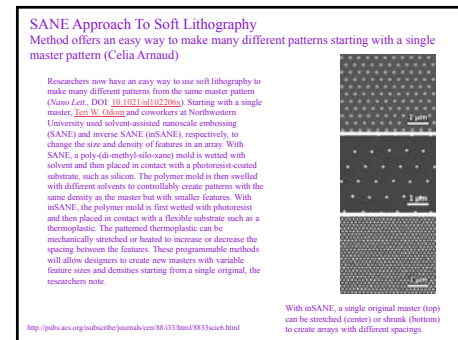
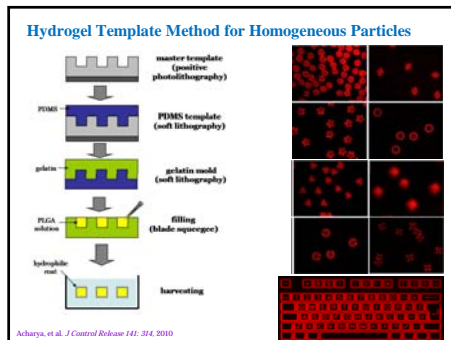
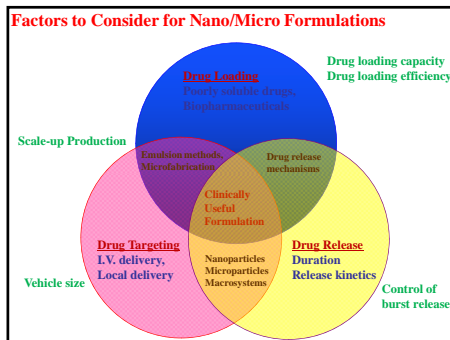
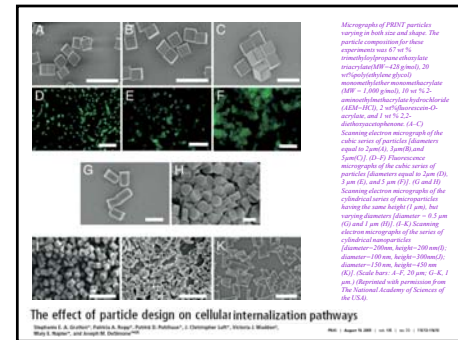
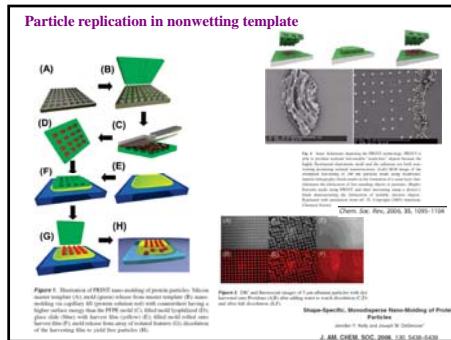
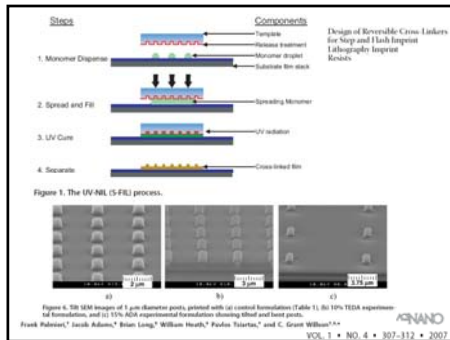
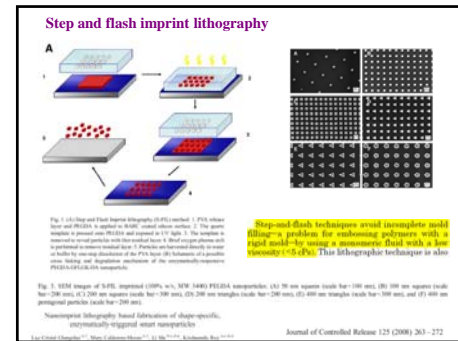
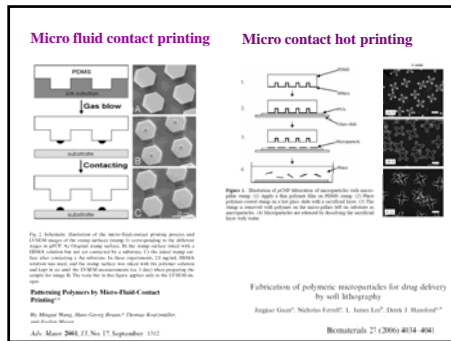
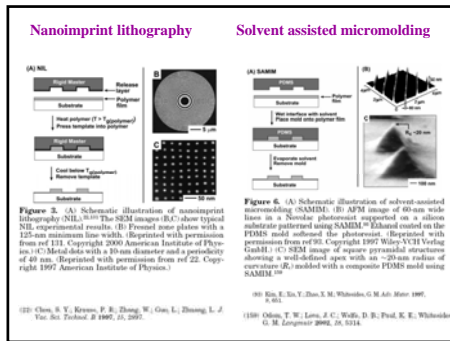
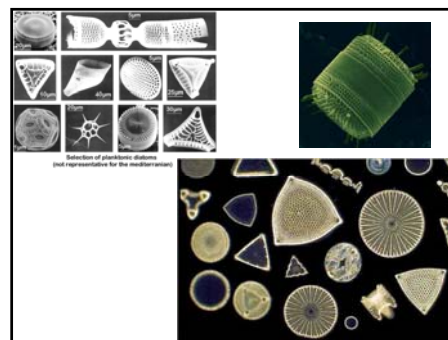
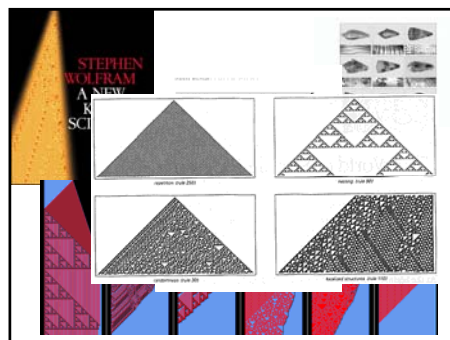
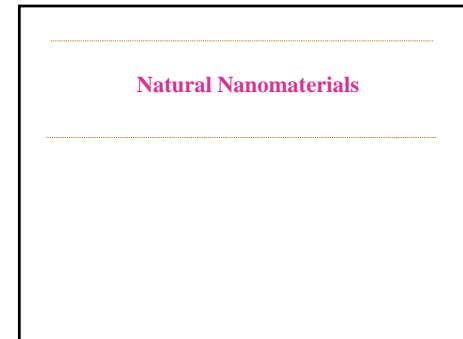
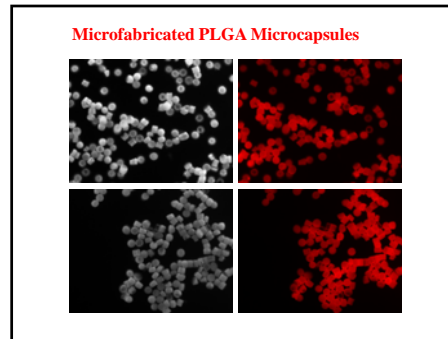
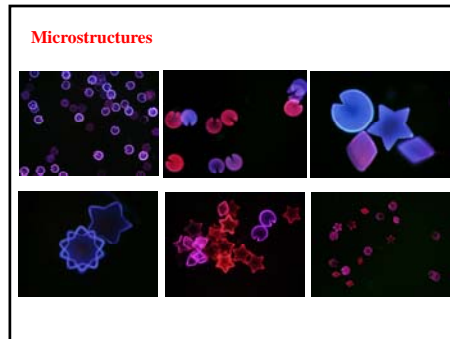
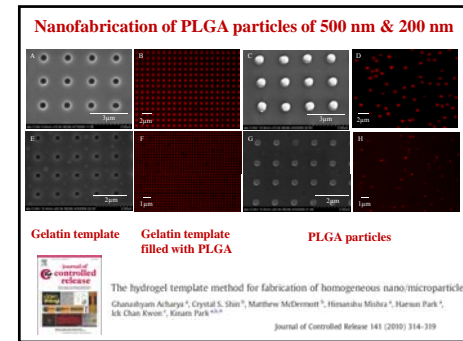
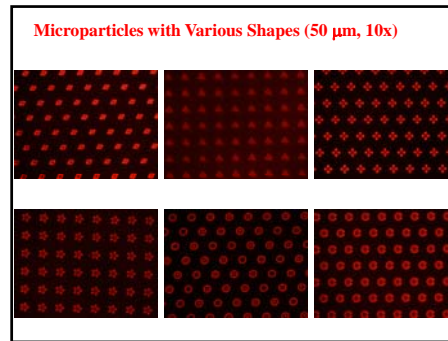
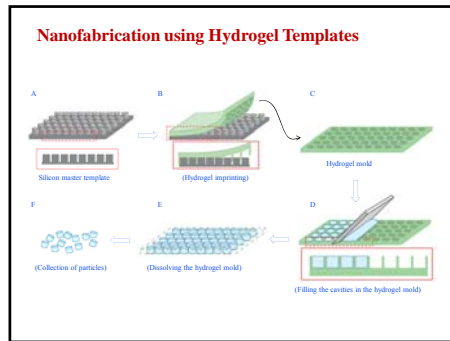


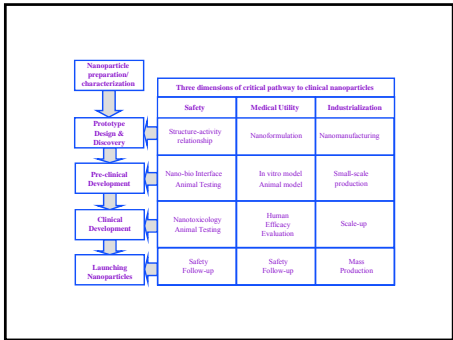
- Fabrication of individual nano/micro structures**
1. Nanoimprint lithography (NIL)
 2. Solvent assisted micromolding (SAMIM)
 3. Micro fluid contact printing (µFCP)
 4. Micro contact hot printing (µCHP)
 5. Step and flash imprint lithography (S-FIL)
 6. Particle replication in nonwetting template (PRINT)
- Limitations**
- Incomplete mold filling (NIL)
 - Formation of a scum layer (SAMIM, PRINT)
 - In situ polymerization (S-FIL, PRINT)
 - No control on thickness (µFCP, µCHP)
 - Multistep process (PRINT)







Nanotoxicity Toxicity of Nanomaterials



This lecture material was prepared by Professor Tamara Minko at Rutgers University, and approval was obtained to use in this class with slight modification.

Professor Tamara Minko, Ph.D.
Interfacial Phenomena

 Department of Pharmaceutics
 Ernest Mario School of Pharmacy
 Rutgers, The State University of New Jersey

minko@cop.rutgers.edu
 732-445-3831 x 214

The contact angle

$\theta = 0^\circ$
complete wetting

$\theta > 90^\circ$

$\theta = 180^\circ$
insignificant wetting

At equilibrium
 $\gamma_s = \gamma_{sl} \cos \theta$

The work of adhesion
 $W_a = \gamma_l + \gamma_s - \gamma_{sl}$
 $= \gamma_l + (\gamma_{sl} + \gamma_l \cos \theta) - \gamma_{sl}$
 $= \gamma_l (1 + \cos \theta)$

The most important action of wetting agents is to lower the *contact angle* between the surface and the wetting liquid. The contact angle θ is the angle between a liquid droplet and the surface over which it contacts.

- ### Interfacial Phenomena
- Interfaces and Surface Tension
 - Adsorption at Liquid Interfaces
 - Adsorption at Solid Interfaces
 - Applications of Surfactants

- ### Interfacial Phenomena
- Interfaces and Surface Tension
 - Adsorption at Liquid Interfaces
 - Adsorption at Solid Interfaces
 - Applications of Surfactants

Interface

An *interface* is the boundary between two phases which exist together.

Classification of Interfaces		
Phase	Type of Interface	Example
Gas-Gas	No interface	
Gas-Liquid	Liquid surface	Body of water exposed to atmosphere
Gas-Solid	Solid surface	Table top
Liquid-Liquid	Liquid-liquid interface	Emulsion
Liquid-Solid	Liquid-solid interface	Suspension
Solid-Solid	Solid-solid interface	Powder particles in contact

Surface Tension

In the bulk, a molecule experiences forces of attraction from neighboring molecules in all directions. The molecule at the interface does not experience the same attraction from the side of the vapor. As the result the energy of the molecule at the interface differs from the energy of bulk molecules. This difference is termed surface free energy (W). This energy should be proportional to the surface area (A) of the interface. The coefficient of proportionality (γ) is termed "surface tension".

Surface Free Energy ~ Surface Area $W = \gamma A$

Surface Tension $\gamma = \frac{W}{A}$

Units: $[\gamma] = \left[\frac{\text{energy}}{\text{area}} \right] = \left[\frac{\text{erg}}{\text{cm}^2} \right] = \left[\frac{\text{dyn} \times \text{cm}}{\text{cm}^2} \right] = \left[\frac{\text{dyn}}{\text{cm}} \right] = \left[\frac{\text{force}}{\text{length}} \right]$

Surface Tension

UNsinkABLE. Surface tension allows water striders to stay high and dry. "Dimples" in the water created by the pressure of the insect's legs make it possible for it to move in a nearly frictionless environment.

The Force of the Surface Tension

The surface tension is a force per unit length and may be illustrated by means of three-sided wire frame (ABCD) across which a movable bar (E-F) is placed. A soap film is formed and stretched by applying a force (f) (such as hanging mass m) to the movable bar, length L , which acts against the surface tension of the soap film. The surface tension of the solution forming the film is then a function of the force that must be applied to break the film over the length of the movable bar in contact with the film. Since the soap film has two liquid-gas interfaces, the total length of the contact is equal to twice the length of the bar ($2L$).

For two interfaces: $\gamma = \frac{\text{force}}{\text{length}} = \frac{f}{2L}$

The downward force is equal to the mass multiplied by the acceleration due to gravity: $f = mg$

Thus: $\gamma = \frac{mg}{2L}$ Where m is the mass required to break a soap film.

$\gamma = \frac{0.50 \text{ g} \times 981 \text{ cm/sec}^2}{2 \times 5 \text{ cm}} = \frac{490.5 \text{ g} \cdot \text{cm}}{10 \text{ cm}} = 49.05 \frac{\text{g} \cdot \text{cm}}{\text{cm}} = 49.05 \frac{\text{dyn} \cdot \text{cm}}{\text{cm}}$

Pressure Differences Across Curved Interfaces

Surface Free Energy $W = \gamma A$
 Surface Area $A = 4\pi r^2$ $W = \gamma 4\pi r^2$

If the radius decreases by dr , the final surface energy:

$$W_1 = \gamma 4\pi r_1^2 = 4\pi\gamma(r - dr)^2 = 4\pi\gamma r^2 - 8\pi\gamma r dr + 4\pi\gamma(dr)^2 \approx 4\pi\gamma r^2 - 8\pi\gamma r dr$$

The decrease in surface free energy: $\Delta W = W_1 - W = \gamma 4\pi r^2 - 4\pi\gamma r^2 - 8\pi\gamma r dr = -8\pi\gamma r dr$

energy change = work = force \times radius change = $\Delta W = P \times A \times (-dr) = P \times 4\pi r^2 \times (-dr)$
 = pressure \times area \times radius change = $-8\pi\gamma r dr = -4P\pi r^2 dr$

$P = \frac{2\gamma}{r}$ Simplified Young-Laplace equation

Another way of expressing surface tension is in terms of the pressure difference that exists across a curved interface. As the radius of a bubble (r) decreases, the pressure (P) of the air inside increases relative to the outside.

Consider two soap bubbles having radii r_1 and r_2 connected via a valve. What happens if we open the valve?

Since the left bubble has a smaller radius and therefore, a higher pressure of the air inside compared with the right bubble, air will move from the smaller bubble to the larger one until the left bubble disappears. NOTE: This is true only if both bubbles were made from the same soap.

$r_1 < r_2$
 $P_1 = \frac{2\gamma}{r_1} > \frac{2\gamma}{r_2} = P_2$
 $P_1 > P_2$

Capillary Rise

Consider a capillary tube of inner radius r immersed in a liquid that wets its surface. The liquid continues to rise in the tube due to the surface tension, until the upward movement is just balanced by the downward force of gravity due to the weight of the liquid.

Capillary Rise

Consider a capillary tube of inner radius r immersed in a liquid that wets its surface. The liquid continues to rise in the tube due to the surface tension, until the upward movement is just balanced by the downward force of gravity due to the weight of the liquid.

Capillary Rise

The surface of the meniscus is curved because a liquid wets the surface of the capillary tube.

Radius of curved meniscus $x = \frac{r}{\cos(\theta)}$

$r = x \cos(\theta)$

$P = \frac{2\gamma}{x} = \frac{2\gamma \cos(\theta)}{r} = \rho g h$

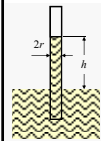
$h = \frac{2\gamma}{\rho g x} = \frac{2\gamma \cos(\theta)}{\rho g r} = \frac{2\gamma}{\rho g r}$

ρ - liquid density g - acceleration of gravity r - inner radius of capillary tube h - height of liquid column

The pressure under the curved surface is directly proportional to the surface tension and inversely proportional to the radius of curved meniscus. From the other hand, this pressure is balanced by the weight of the liquid, which is equal $\rho g h$. Finally, the height of the capillary rise is directly proportional to the surface tension and inversely proportional to the liquid density, acceleration of gravity and the radius of capillary tube.



Measurement of Surface Tension: Capillary Rise Method



$$h = \frac{2\gamma}{\rho g r}$$

ρ – liquid density
 g – acceleration of gravity
 r – inner radius of capillary tube
 h – height of liquid column

$$\gamma = \frac{r h \rho g}{2}$$

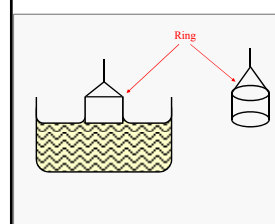
Example. A sample of distilled water rose to a height (h) of 14.84 cm at 20° C in a capillary tube having an inner radius (r) of 0.01 cm. The water density (ρ) is 1 g/cm³. What is the surface tension of water at this temperature?

$$h = 14.84\text{cm} \quad r = 0.01\text{cm} \quad \rho = 1\text{g/cm}^3$$

$$\gamma = \frac{r h \rho g}{2} = \frac{1}{2} \times 0.01\text{cm} \times 14.84\text{cm} \times 1\text{g/cm}^3 \times 981\text{cm/sec}^2$$

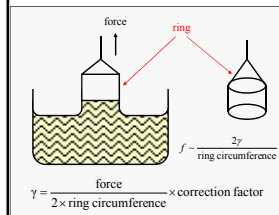
$$\gamma = 72.8\text{g/sec}^2 = 72.8\text{g} \cdot \text{cm}/(\text{sec}^2 \cdot \text{cm}) = 72.8\text{dynes/cm}$$

Measurement of Surface Tension: The DuNouy Ring Method



The principle of this method depends on the fact that the force necessary to detach a platinum-iridium ring immersed at the surface is proportional to the surface tension. In fact, the instrument measures the weight of liquid pulled out of the plane of the interface immediately before the ring becomes detached.

Measurement of Surface Tension: The DuNouy Ring Method

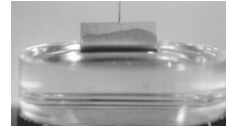


The principle of this method depends on the fact that the force necessary to detach a platinum-iridium ring immersed at the surface is proportional to the surface tension. In fact, the instrument measures the weight of liquid pulled out of the plane of the interface immediately before the ring becomes detached.

A correction factor is necessary because simple theory does not take into account certain variables such as the radius of the ring, the radius of the wire used to form the ring, and the volume of liquid raised out of the surface.

$$\gamma = \frac{\text{force}}{2 \times \text{ring circumference}} \times \text{correction factor}$$

Semi-Automatic Surface Tensiometer



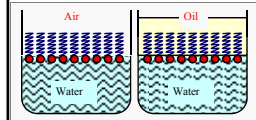
The new ST-PLUS Semi-automatic Surface Tensiometer from Tanteq, Inc. offers advanced, microprocessor-based measurement using either the Wilhelmy Plate or DuNouy Ring Methods. The Wilhelmy plate method is based on the measurement of the force necessary to detach a plate from the surface of a liquid.

Interfacial Phenomena

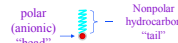
- Interfaces and Surface Tension
- Adsorption at Liquid Interfaces
- Adsorption at Solid Interfaces
- Lung Surfactant

Surface-Active Agents

Surface-Active Agents or *Surfactants* are molecules and ions that are adsorbed at interfaces. They are *amphiphiles*, which means that the molecules or ions have a certain affinity for both polar and nonpolar solvents.

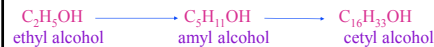


Surfactants usually have polar groups and nonpolar groups. For example, fatty acids have a polar "head" and a nonpolar "tail".



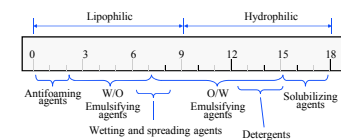
It is the amphiphilic nature of surface-active agents that causes them to be adsorbed at interfaces. In an aqueous dispersion of an amphiphile, the polar groups ("heads") are able to associate with the water molecules. The nonpolar portion of the molecules are rejected. As a result, the amphiphile is adsorbed at the interface. Adsorption of amphiphile at a water-air or water-oil interface gives a similar result.

Hydrophile-Lipophile Classification



Depending on the number and nature of the polar and nonpolar groups present, the amphiphile may be predominantly *hydrophilic* ("water loving"), *lipophilic* ("oil-loving"), or somewhere between these two extremes. For example, straight-chain alcohols, amines, and acids are amphiphiles that change from being predominantly hydrophilic to lipophilic as the number of carbon atoms in the alkyl chain is increased. Thus, ethyl alcohol is miscible with water in all proportions. The aqueous solubility of amyl alcohol is much reduced, while cetyl alcohol is almost insoluble in water.

HLB (Hydrophilic-Lipophilic Balance)

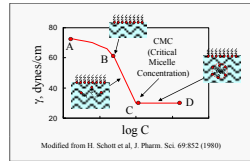


Griffin devised an arbitrary scale of values to serve as a measure of hydrophilic-lipophilic balance (HLB) of surface-active agents. The higher the HLB of an agent, the more hydrophilic it is. By means of this number system, it is possible to establish an HLB range of optimum efficiency for each class of surfactant. For example most of antifoaming agents have a HLB between 1 and 3; water/oil emulsifying agents – between 3 and 8; wetting and spreading agents – between 7 and 9; oil/water emulsifying agents – between 8 and 16; detergents – between 13 and 16; solubilizing agents – between 16 and 19.

Monolayers

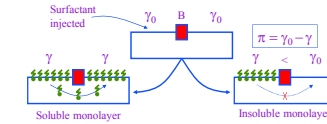
Adsorbed materials are divided into two groups: those that form “soluble” monolayers and those that form “insoluble” films. The distinction is made on the basis of the solubility of the adsorbate in the liquid subphase.

Soluble Monolayers



The addition of amphiphiles (soluble surfactants) to a liquid system leads to a reduction in surface tension. If surface tension is plotted against the logarithm of surfactant concentration, the three segments might be separated. The initial curved segment A-B is followed by a linear segment, B-C, along which there is a sharp decrease in surface tension. Near point B the monolayer is formed and molecules are closely packed at the surface. The point C corresponds to the critical micelle concentration (CMC) the concentration at which micelles form in the solution. Beyond the CMC the line becomes horizontal, further additions of surfactant no longer being accompanied by a decrease in surface tension.

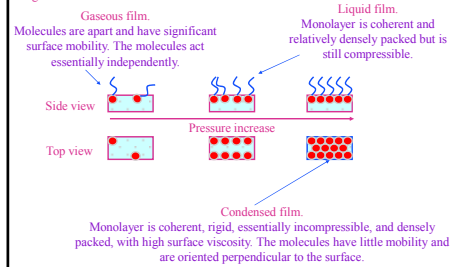
Insoluble Monolayers



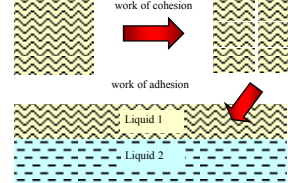
Consider a reservoir that has a movable barrier (B). The reservoir is filled with pure water. The surface tension of the water on each side of the barrier will be the same (γ_0). A quantity of surfactant is added to one side of the reservoir. If the surfactant is soluble, surfactant molecules will dissolve in the water and be adsorbed on the other side of the barrier. After reaching equilibrium, the surface tensions of both sides of the barrier will be equal. If the surfactant is insoluble, the surface tension of the side with surfactant will decrease to γ , while the other side will remain that of pure water, γ_0 . The surface pressure of a monolayer film, π , is defined as the difference between the surface tension of the pure supporting liquid, γ_0 , and that of the liquid with an adsorbed film, γ .

Insoluble Monolayers

Insoluble monolayer films exhibit characteristics that can be equated to the solid, liquid and gaseous states of matter.



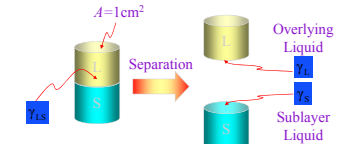
Spreading



The spreading of one liquid over the another requires that two forces be in cooperation:

- the work of cohesion, the work required to separate the molecules of the spreading liquid
- the work of adhesion, the work required to attract the unlike molecules

Work of Adhesion

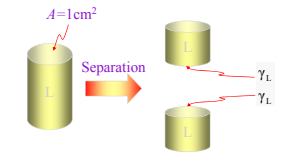


$$\text{Work} = \text{Surface tension} \times \text{Unit area change} (= 1)$$

$$\text{Work of adhesion } W_a = \gamma_L + \gamma_S - \gamma_{LS}$$

The work of adhesion is the energy required to break the attraction between the unlike molecules. Consider a hypothetical cylinder with cross-section area 1 cm^2 of the sublayer liquid S overlaid with a similar section of the spreading liquid L. The work required to separate the two sections of liquid is equal numerically to the newly created surface tensions minus the interfacial tension that has been destroyed in the process.

Work of Cohesion



$$\text{Work} = \text{Surface tension} \times \text{Unit area change} (= 1)$$

$$\text{Work of cohesion } W_c = 2\gamma_L$$

The work of cohesion is the work required to separate the molecules of the spreading liquid so that it can flow over the sublayer. Obviously, no interfacial tension exists between the like molecules of the liquid. When the hypothetical 1 cm^2 cylinder is divided, two new surfaces are created with the same surface tension. Therefore, the work of cohesion is equal numerically to the two newly created surface tensions.

Spreading Coefficient

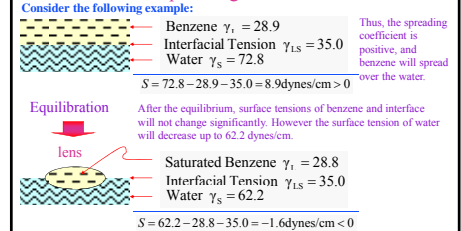
Spreading coefficient = Work of adhesion – Work of cohesion (per unit of surface)

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

If $S > 0$, the liquid will spread over another liquid surface.

If $S < 0$, the liquid will coalesce of the excess material into a lens.

Spreading Coefficient



In this case spreading coefficient will be negative, and saturated benzene will form a lens. While benzene spreads initially on water, at equilibrium a saturated monolayer is formed with the excess benzene (saturated with water) forming a lens.

Interfacial Phenomena

- Interfaces and Surface Tension
- Adsorption at Liquid Interfaces
- Adsorption at Solid Interfaces
- Lung Surfactant

The Solid-Gas Interface

The degree of adsorption of a gas by a solid depends on:

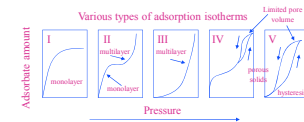
- ❖ the chemical nature of the *adsorbent* (the material used to adsorb the gas) and the *adsorbate* (the substance being adsorbed);
- ❖ the surface area of the adsorbent;
- ❖ the temperature;
- ❖ the partial pressure of the adsorbed gas.

The types of adsorption:

- ❖ *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 may be desorbed from a solid by increasing the temperature and reducing the pressure.
- ❖ *Chemical adsorption* or *chemisorption*, in which the adsorbate is attached to the adsorbent by primary chemical bonds, is irreversible.

Adsorption isotherms

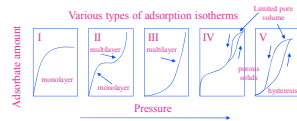
Adsorption isotherm is the relationship between the amount of gas physically adsorbed on a solid and the equilibrium pressure or concentration at constant temperature. There are five types of isotherms:



- ❖ Type I describes the adsorption of gas by monolayers (Freundlich or Langmuir isotherms) or chemisorption.
- ❖ Type II – physical adsorption onto nonporous solids to form a monolayer followed by multilayer formation.
- ❖ Type III – occurs in porous solids when the forces of monomolecular adsorption are small; these are very rare types of isotherms.

Adsorption isotherms

Adsorption isotherm is the relationship between the amount of gas physically adsorbed on a solid and the equilibrium pressure or concentration at constant temperature. There are five types of isotherms:



- ❖ Type IV is typical of adsorption onto porous solids; it includes a monolayer formation on the surface of a solid followed by the multilayer formation and capillary condensation within the pores of the solid.
 - ❖ Type V is similar to type III with limited pore volume.
- Types IV and V frequently involve hysteresis.

Activated Charcoal

Diameter D	Volume $V = \pi D^3/6$	Surface $A = \pi D^2$
1.2 cm	1 cm ³	~5 cm ²
1 cm	1 cm ³	~6 cm ²
0.01 cm	1 cm ³	~500 cm ²
10 ⁻⁴ cm	1 cm ³	~600 m ²

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. Consider the following example: a sphere with the diameter of 1.2 cm has a volume of 1 cm³ and a surface area of 5 cm². If the sphere is divided into two spheres, each with a diameter of 1 cm, together they will have the same volume of 1 cm³ but an increased surface area of 6 cm². If we continue to divide the spheres and finally mill them to particles with diameters of about 10⁻⁴ cm, the total surface area will increase to hundreds of square meters. Modern activated charcoal has thousands of square meters of active surface area per 1 g of mass. It is used as an antidote for poisonings by many substances including drugs (sulfonylureas, acetaminophen, phenobarbital, etc.).

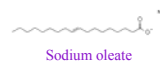
Wetting

Adsorption at solid interfaces is involved in the phenomena of wetting and detergency. It also aids in displacing an air phase at the surface, replacing it with a liquid phase. Examples of the application of wetting to pharmacy and medicine include:

- ❖ the displacement of air from the surfaces of sulfur, charcoal, and other powders for the purpose of dispersing these drugs in liquid vehicles;
- ❖ the displacement of air from the matrix of cotton pads and bandages so that medicinal solutions may be adsorbed for application to various body areas;
- ❖ the displacement of dirt and debris by the use of detergents in the washing of wounds;
- ❖ the application of medical lotions and sprays to the surface of the skin and mucous membranes.

Applications of surfactants

Soaps and detergents

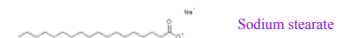
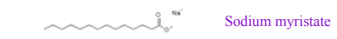
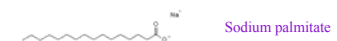
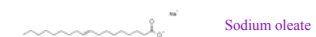


All of the soaps (sodium oleate etc) are fatty acid salts (anionic surfactant). They are characterized by:

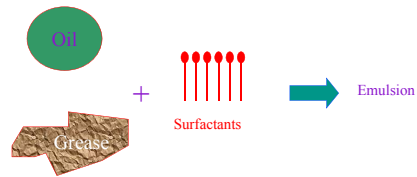
- a long hydrocarbon chain, which may be monounsaturated (i.e., has one double bond, like sodium oleate), polyunsaturated (i.e., more than one double bond) or saturated (i.e. no double bonds)
- a carboxylate group at the end

Any surfactant that is not a soap is a detergent.

Common soaps

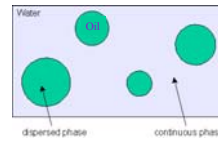


The cleaning action of soaps and detergents



The cleaning action of soaps and detergents is based on the property known as detergency. To remove oils and greases, soaps and detergents help make an emulsion.

Surfactants and emulsions



Possibly the most important industrial role for surfactants is the formation of emulsions. An emulsion is a dispersion of one liquid in a second, immiscible liquid. If you ever shaken up salad dressing, you have made emulsion. Milk and cream are emulsions, as are medicinal creams such as moisturisers.

Emulsions are multiphase systems, even though they often look like they are just one phase. The phases in an emulsion are normally called the continuous phase and the dispersed phase.

Detergents

Detergents are surfactants that are used for the removal of dirt. Detergency is a complex process involving the removal of foreign matter from surfaces. The process includes the following main steps:

