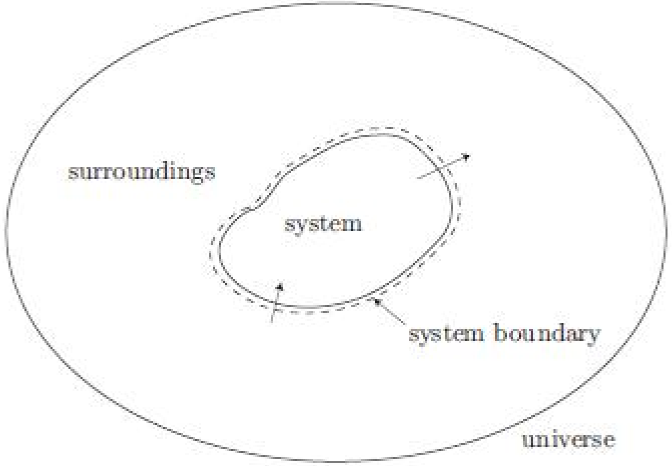
Review of Thermodynamics

- Thermodynamics was developed by engineers to describe the conversion of chemical energy stored in fossil fuel into heat and useful work.
  - The study of the relationship between work, heat, and energy.
  - Deals with the conversion of energy from one form to another.
  - Deals with the interaction of a system and it surroundings.



System - identifies the subject of the analysis by defining a boundary

Surroundings - everything outside the system boundary.

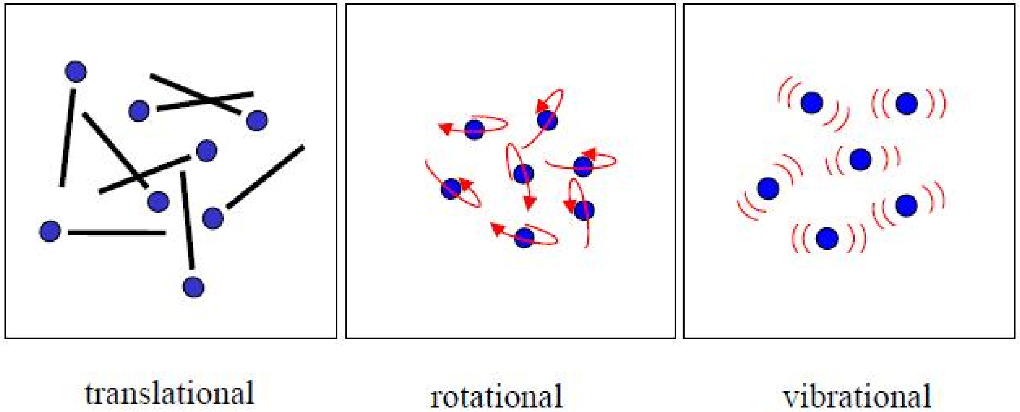
Forms of Energy

– **Mechanical Energy of an Object**

- **Kinetic Energy =** $\frac{1}{2}mv^2$
- **Potential Energy=** mgh
- **Total Energy = KE + PE = Constant**

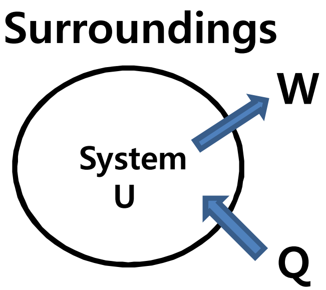
\- **Internal Energy (U)**

- **Attributed to the motions and configuration of the individual molecules, atoms and subatomic particles making up the matter in the system.**
- **Motions are described as as translational, rotational and vibrational.**



- **indirectly measurable by changes in <u>Temperature</u>, <u>Pressure</u> and <u>Density</u>**

Work and Heat



Energy transfer occurs between the system and the surroundings in the form of Heat and Work

Work (W) → refers to mechanical work
Heat (Q) → refers to energy transferred from a hot to a cold object

First Law of Thermodynamics

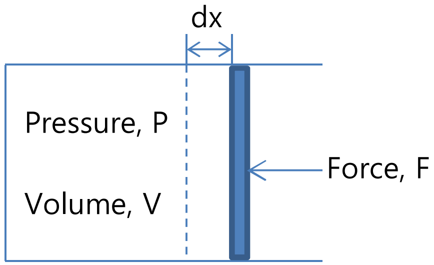
Law of conservation of energy → the total quantity of energy is constant and when energy disappears in one form it appears simultaneously in another form.

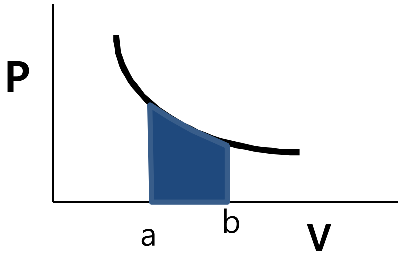
$$\triangle U = Q - W$$
$$dU = dQ - dW$$

U: Internal Energy
Q: Heat Flow from surroundings
W: Work done by the system (+)
Work done on the system (-)

Mechanical Work

- **Mechanical Work, dW = F dx = PA dx = PdV**



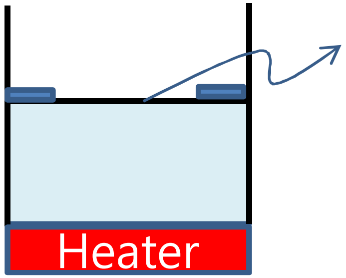


$$W = \int_{V_a}^{V_b} PdV$$

- Work done on a system is positive, and work done by the system as negative.
- An example of work by the system is the expansion of a cylinder against the atmosphere.

$$W = -\int_{V_a}^{V_b} PdV$$

Heat Exchanged at Constant Volume



Fixed
Volume constant

$$Q \propto \Delta T \quad \rightarrow Q = C_V \Delta T$$

- Heat Capacity at Constant Volume

$$C_V(T, P) = \frac{dQ}{dT}$$

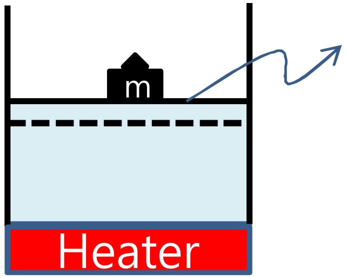
C_V: - amount of heat needed to raise the temperature of a mole of substance by one degree, while keeping the volume constant.
- depends on the temperature T, and the pressure P

- For a system doing only PV work:

$dU = dQ - PdV$

at constant volume, $dU = dQ$

Heat Exchanged at Constant Pressure



Freely movable
Pressure stays constant (against the same weight on the piston)

$$Q = C_P \Delta T$$

- Heat Capacity at Constant Pressure

$$C_P(T, P) = \frac{dQ}{dT}$$

C_P: - amount of heat needed to raise the temperature of a mole of substance by one degree, while keeping the pressure constant.
- depends on the temperature T, and the pressure P

$C_P > C_V$: Temperature will rise more if the volume of the gas (rather than pressure) is held constant.

$C_P - C_V = R \; for \; Ideal \; Gas$

Enthalpy, H

- Another expression for total system energy is Enthalpy (H):
- Define

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

- For mechanical work, $dU=dQ-PdV$

$$dH = dQ + VdP$$

- At constant pressure, $dH=dQ$

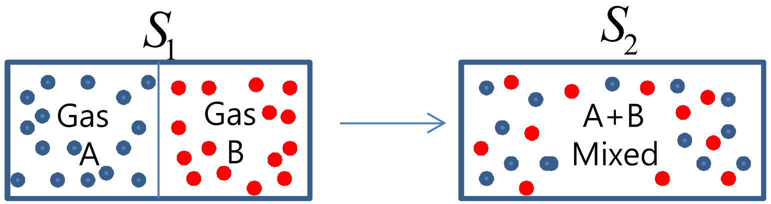
$$Cv = \left(\frac{\partial U}{\partial T}\right)_V \qquad C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

Second Law of Thermodynamics

- Spontaneous Process and Entropy
  - Rocks fall down, Heat flows from a hot to a cold, Chemical reactions goes in one direction

- **Entropy:** Thermodyamic quantity that is a measure of the randomness or disorder in a system, S

- A process occurs naturally as a result of an overall increase in disorder



$$S_2 - S_1 = \Delta S > 0$$

For spontaneous Change

- `

- Total entropy of a system and its surroundings always increases.

$$\Delta S_{univ} \geq 0$$

- ➢ First Law: Energy of the universe is conserved
- ➢ Second Law: Entropy of the universe is increasing

- ➢ Isolated System: $\Delta U_{system} = 0,\ \Delta S_{system} \geq 0$

Entropy

- ***Entropy (S)*** **is that part of the total energy of the system that is not available to do useful work.**

DEF Definition of the change of entropy:

$$\mathrm{d}S = \frac{\delta q_{\mathrm{rev}}}{T}$$

δq_{rev} heat exchange of the system in a reversible process

T temperature of the heat exchange

entropy is a state function and extensive

Unit: J/K

Interpretation:

Well ordered system:	small entropy	(*e.g.* crystal)
disordered system:	large entropy	(*e.g.* gases)

In spontaneous processes entropy increases or remains constant.

Combining 1st and 2nd Laws

- $dU = dq + dw$
  $= dq - PdV + dw'$ (w': other kinds of work)
  $= TdS - PdV + dw'$

- $dH = dq + VdP$ (mechanical work only)
  $= TdS + VdP$

Helmholtz free energy $F(T,V)$:

$F = U - TS$

$dF = dU - SdT - TdS$

$= -SdT - PdV$

Gibbs Free Energy, G

- The Gibbs Free energy is that portion of the total system energy that is available for useful work.

- Define $G = H - TS$

  $$\begin{aligned} G &= H - TS \\ &= U + PV - TS \\ dG &= dU + PdV + VdP - TdS - SdT \\ &= TdS - PdV + dw' + PdV + VdP - TdS - SdT \\ &= VdP - SdT + dw' \end{aligned}$$

- in the absence of other work, $dG = VdP - SdT$

- at constant P and T, $dG = dw'$
  - The change of Gibbs free energy from the actual state till reaching the equilibrium at constant pressure and temperature provides the maximal work that the system can do

- At equilibrium, $dG=0$

Chemical Potential

$\mu = \frac{G}{n}$

G: Gibbs Free Energy
n: no. of moles

μ: most important function in thermodynamics
(intensive property)

$$G = H - TS \qquad \frac{G}{n} = \frac{H}{n} - T\frac{S}{n} \longrightarrow \mu = h - Ts$$

$$dG = -SdT + VdP \longrightarrow \mu = -sdT + vdP$$

Chemical Potential of an Ideal Gas

$d\mu = -sdT + vdP$

At constant temperature

$d\mu = vdP$ $\qquad$ $\mu(T, P) - \mu(T, P_o) = \int_{P_o}^{P} vdP$

$v = \frac{RT}{P}$ $\longrightarrow$ $\mu(T, P) = \mu(T, P_o) + RTln\frac{P}{P_o}$

If P_o is 1, $\qquad$ $\mu(T, P) = \mu^o + RTlnP$

Real Gas: $\qquad$ $\mu(T, P) = \mu^o + RTlnf$ $\qquad$ f: fugacity

Similarly Real solution: $\qquad$ $\mu(T, P) = \mu^o + RTlna$ $\qquad$ a: activity

Chemical Potential of a Compound in a Mixture

- Need to know the number of moles n_i of each component in a mixture

$$molar\ fraction:\ \ x_i = \frac{n_i}{n} \qquad n = \sum_{i=1}^{k} n_i\ , \qquad k: number\ of\ components$$

$$G = f(T, P, n_1, n_2, \dots \dots, n_k) \qquad n_i\ can\ be\ changed\ independently.$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3..} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3..} dn_2 + \dots..$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \sum_{i=1}^{k} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} dn_i$$

Chemical Potential of a Compound in a Mixture

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \sum_{i=1}^{k} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} dn_i$$

$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \mu_i$ Chemical potential of component *i* in a multi-component system: Change in G with the number of moles of compound *i* at const. T and P

$$dG = -SdT + VdP + \sum_{i=1}^{k} \mu_i \, dn_i$$

In analogy

$$dF = -SdT - PdV + \sum_{i=1}^{k} \mu_i \, dn_i$$

$$dU = TdS - PdV + \sum_{i=1}^{k} \mu_i \, dn_i$$

Systems Involving Interface

$$G = f(T, P, n_1, n_2, \ldots\ldots, n_k,\text{ A})$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,ni,A} dT + \left(\frac{\partial G}{\partial P}\right)_{T,ni,A} dP + \sum_{i=1}^{k}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j,A} dn_i + \left(\frac{\partial G}{\partial A}\right)_{P,T,ni} dA$$

define $\gamma = \left(\frac{\partial G}{\partial A}\right)_{P,T,n_i}$

$$dG = -SdT + VdP + \sum_{i=1}^{k} \mu_i\, dn_i + \gamma dA$$

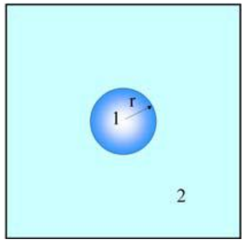
Also,

$$dF = -SdT - PdV + \sum_{i=1}^{k} \mu_i\, dn_i + \gamma dA$$

$$dU = TdS - PdV + \sum_{i=1}^{k} \mu_i\, dn_i + \gamma dA$$

Curved Surface

- Consider two phases 1 and 2, separated by a surface of area A, in equilibrium.



$$dF = -SdT - PdV + \sum_{i=1}^{k} \mu_i \, dn_i + \gamma dA$$

Equilibrium at constant T and composition

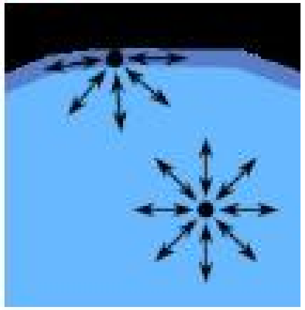
$$0 = -P_1 dV_1 - P_2 dV_2 + \gamma dA$$

Since $dV_1 = -dV_2$ $\quad (P_1 - P_2) dV_1 = \gamma dA$

$$dV = 4\pi r^2 dr, \qquad dA = 8\pi r dr$$

$$(P_1 - P_2) = \frac{2\gamma}{r} : \qquad Laplace\ Eq.$$

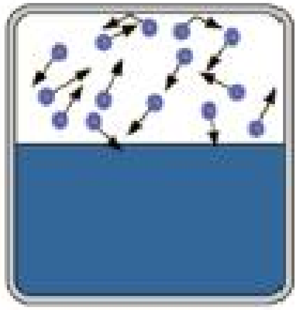
Vapour pressure of curved surfaces



convex curved surfaces (∩) : each surface molecule has (on average) less neighbours compared to a flat surface.

⇒ these molecules are less anchored by the neighbours
⇒ can fly away more easiliy due to the thermic movements

Vapour pressure depends on the curvature of the surface:
Compared to a flat surface,
higher vapour pressure belongs to the convex (∩) surface and
lower vapour pressure belongs to the concave (∪) surface.



Vapour pressure p of a curved surface (**Kelvin equation**):

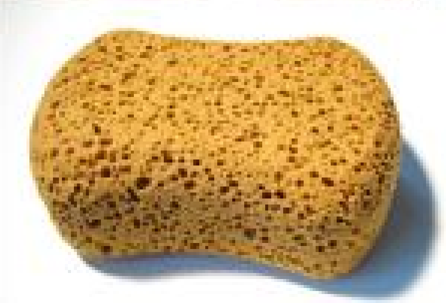
$$\ln \frac{p}{p^*} = \pm \frac{2\gamma V_m}{RTr}$$

p^*	vapour pressure of the planar surface
γ	liquid–vapour surface tension
V_m	molar volume of the liquid
r	curvature radius of the liquid
sign +:	convex (∩) surface
sign –:	concave (∪) surface

Vapour pressure of curved surfaces – strange consequences

In a closed system the smaller droplets evaporate onto larger droplets

Water droplets on the inside wall of a mineral water bottle evaporate to the bulk of the water, having flat surface.

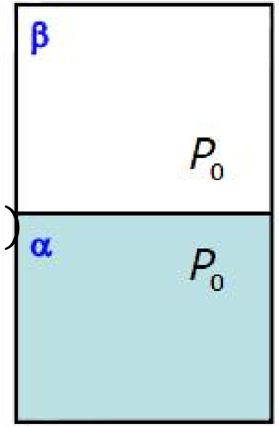


Water evaporates slowly from a sponge because of the concave water surfaces in the holes.

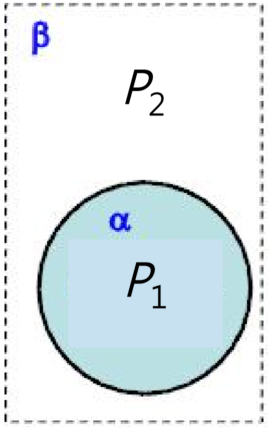
Vapour pressure of liquid droplets

one-component system: liquid (α) – gas (β) equilibrium

$$\mu^{\alpha}(P_0) = \mu^{\beta}(P_0)$$



$$\mu^{\alpha} = \mu^{\beta}$$



$$\mu^{\alpha}(P_1) = \mu^{\beta}(P_2)$$

$$d\mu = vdP$$

(at constant T)

$$\mu(T,P) = \mu(T,P_o) + RTln\frac{P}{P_o}$$

$$\mu^{\alpha}(P_1) - \mu^{\alpha}(P_0) = \mu^{\beta}(P_2) - \mu^{\beta}(P_0)$$

$$v(P_1 - P_0) = RTln\frac{P_2}{P_0} \qquad RTln\frac{P_2}{P_0} = \frac{2\gamma v}{r}: \qquad Kelvin\ Equation$$

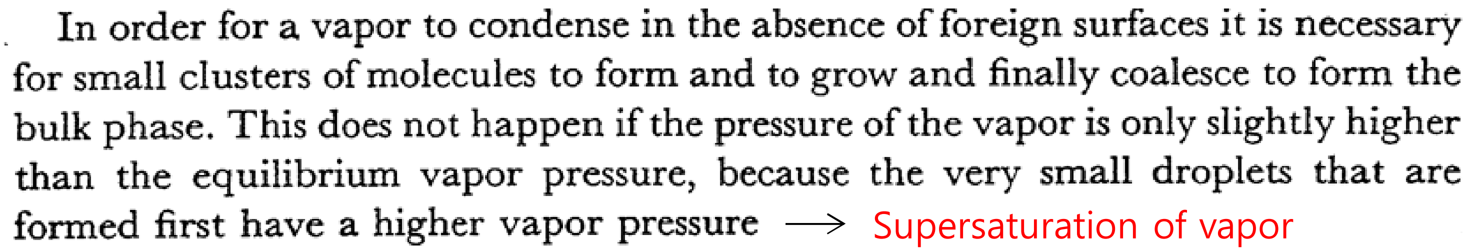
v: molar volume of the liquid

Vapor pressure over a convex surface > that over flat surface

For water droplets:

r, nm	P_r/P_o
100	1.01
10	1.1
1	3.0

The smaller the particle, the higher the vapor pressure

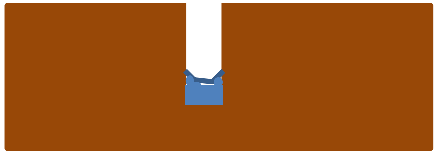


In order for a vapor to condense in the absence of foreign surfaces it is necessary for small clusters of molecules to form and to grow and finally coalesce to form the bulk phase. This does not happen if the pressure of the vapor is only slightly higher than the equilibrium vapor pressure, because the very small droplets that are formed first have a higher vapor pressure → Supersaturation of vapor

An example of supersaturation of vapor is in the cloud formation. In forming clouds, the rise of warm humid air allows water from a surface of a liquid i.e. ocean to evaporate and rise into the atmosphere. As it rises, the atmosphere becomes cooler and so the water vapor would condense. Small group of dispersed molecules are gathered to form water drops. As because of the small droplets have a high vapor pressure, they tend to evaporate and disappear. Hence, once the droplets are formed from condensation of water vapor, they would evaporate again. One aspect of the Kelvin equation is that cloud formation is not seen because clouds are made of water droplets having a small radius which consequently disappear

When the curvature is negative (i.e. concave) then a lowering of the vapor pressure is predicted since r becomes negative.

$$RTln\frac{P_2}{P_0} = -\frac{2\gamma v}{r}$$



Vapor condenses in small capillaries
To remove water moisture from pores, heat greater than 100°C must be Applied to the porous solids

The same relation can be derived for the dependence of the solubility on surface curvature:

$$RTln\frac{S_C}{S_0} = \frac{2\gamma v}{r}$$

where *Sc* is the solubility of a curved solid surface, S_0 is the solubility of a flat surface. This equation is also known as the Gibbs–Thompson relation.

Correspondingly, the solubility of a solid with a convex surface is greater than the solubility of flat surfaces of the same substance.

Also, the Kelvin equation defines the direction of the transport of the substance (from greater to lesser values of *P* and *C*) in the process of the system’s transition to a state of thermodynamic equilibrium. In particular, this leads to a situation in which large drops or particles grow as a result of the evaporation or solution of smaller drops or particles.

- One of the mechanism for emulsion breakdown

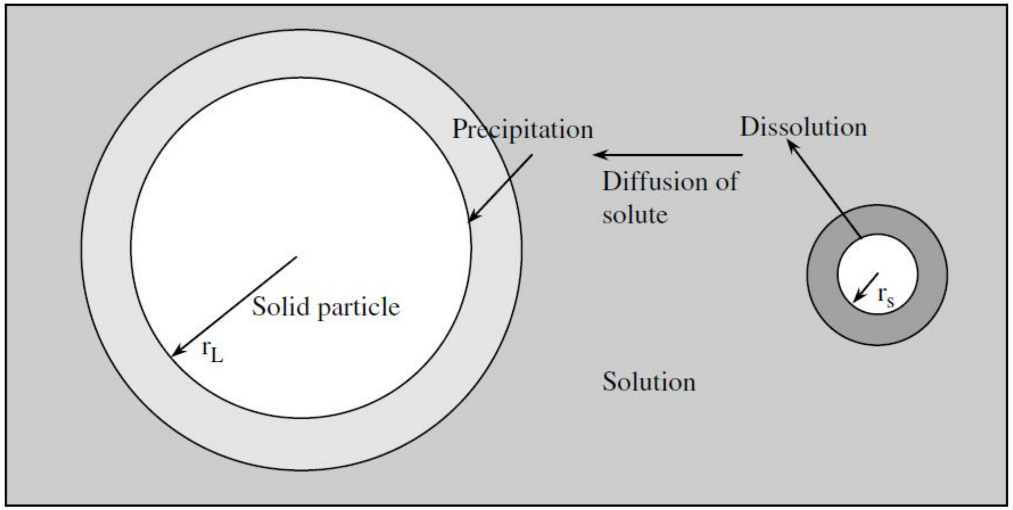
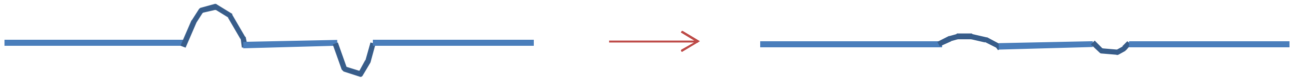


Figure 2.13. Schematic illustrating the Ostwald ripening processing. Smaller particle has a larger solubility or vapor pressure due to its larger curvature, whereas the larger particle possesses a smaller solubility or vapor pressure. To maintain the local concentration equilibrium, smaller particle would dissolve into the surrounding medium; solute at proximity of smaller particle diffuses away; solute at proximity of larger particle would deposit. The process would continue till disappearance of the smaller particle.

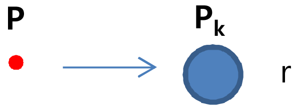


Uneven surfaces are smoothed out by solution of the protrusions and filling of the depressions.

Noticeable differences in pressure and solubility are found only for sufficiently small *r*. Therefore, the Kelvin equation is used most widely to characterize the state of small entities (particles of colloidal systems and nucleations of the new phase) and in the study of capillary phenomena.

Nucleation

Let's consider the energy cost of nucleating a drop out of equilibrium



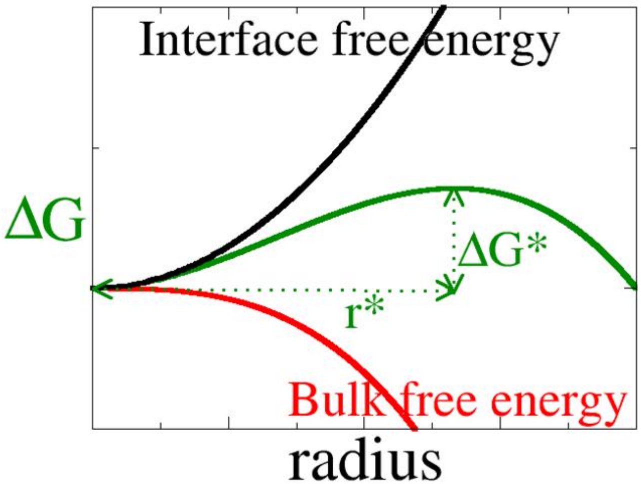
Free energy change for the condensation of n moles vapor at a vapor pressure P, into a drop, which has a vapor pressure P_k.

$$\Delta G = nRTln\frac{P_k}{P} + 4\pi r^2\gamma = -nRTln\frac{P}{P_k} + 4\pi r^2\gamma$$

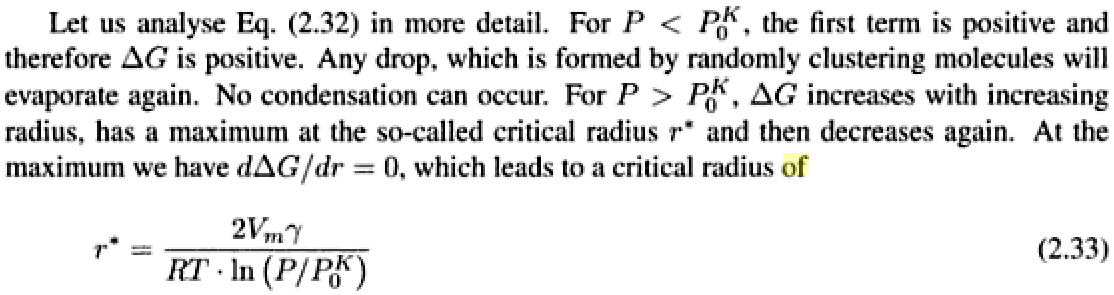
$$n = \frac{4}{3}\pi r^3/V_m \qquad V_m\text{: molar volume}$$

$$\Delta G = -\frac{4\pi r^3}{V_m}RTln\frac{P}{P_k} + 4\pi r^2\gamma$$

The first term shows the energy gain of creating a new volume and the second term shows the energy loss due to surface tension of the new interface.



$$\Delta G = -\frac{4\pi r^3}{V_m} RT ln \frac{P}{P_k} + 4\pi r^2 \gamma$$



Let us analyse Eq. (2.32) in more detail. For $P < P_0^K$, the first term is positive and therefore ΔG is positive. Any drop, which is formed by randomly clustering molecules will evaporate again. No condensation can occur. For $P > P_0^K$, ΔG increases with increasing radius, has a maximum at the so-called critical radius r^* and then decreases again. At the maximum we have $d\Delta G/dr = 0$, which leads to a critical radius of

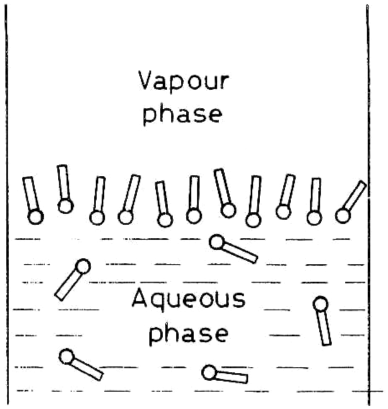
$$r^* = \frac{2V_m\gamma}{RT \cdot \ln\left(P/P_0^K\right)} \tag{2.33}$$

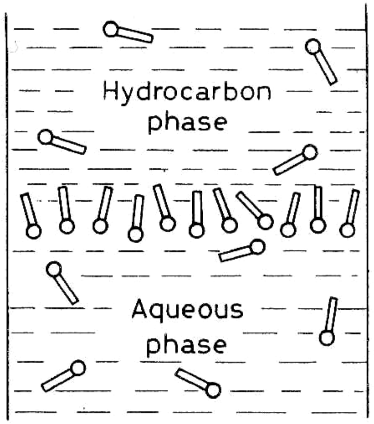
It costs free energy to add molecules to this cluster until the radius reaches critical radius because $\frac{dG}{dr} > 0$.

Addition of new molecules to clusters larger than this critical radius releases, rather than costs, available work. In other words, at that point, growth of the cluster is no longer limited by nucleation

Adsorption at Interface

- Materials such as short-chain fatty acids and alcohols are soluble in both water and oil (e.g. paraffin hydrocarbon) solvents. The hydrocarbon part of molecule is responsible for its solubility in oil, whilst the polar –COOH or –OH group has sufficient affinity to water to drag a short-length non-polar hydrocarbon chain into the aqueous solution with it.
- When these molecules become located at an air-water or an oil-water interface, they are able to locate their hydrophilic head groups in the aqueous phase and allow the lipophilic hydrocarbon chains to escape into the vapor or oil phase.
- The strong adsorption of such materials at surfaces or interfaces in the form of an oriented monomolecular layer (or monolayer) is termed surface activity.
- Surface activity is a dynamic phenomenon, since the final state of a surface or interface represents a balance between this tendency towards adsorption and the tendency towards complete mixing due to the thermal motion of the molecules.





Adsorption at Interface

- The tendency of surface-active molecules to pack into an interface favors an expansion of the interface; this must, therefore, be balanced against the tendency for the interface to contract under normal surface tension forces.
- If π is the expanding pressure (or surface pressure) of an adsorbed layer of surfactant, then the surface (or interfacial) tension will be lowered to a value $\gamma = \gamma_0 - \pi$

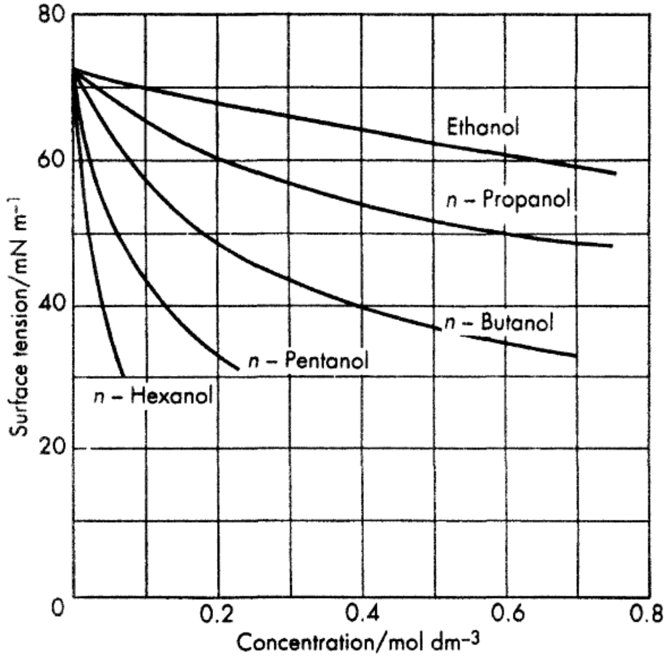


Figure 4.10 Surface tension of aqueous solutions of alcohols at 20°C

The longer the hydrocarbon chain, the greater is the tendency for the alcohol molecules to adsorb at the air-water interface and, hence, lower the surface tension.

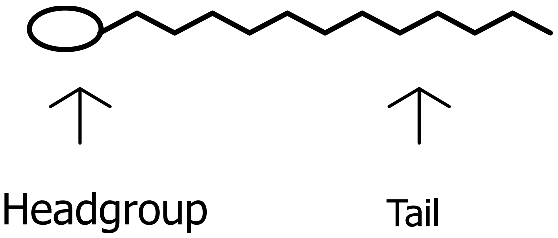
Traube’s Rule: 1/3 conc for each CH_2 group

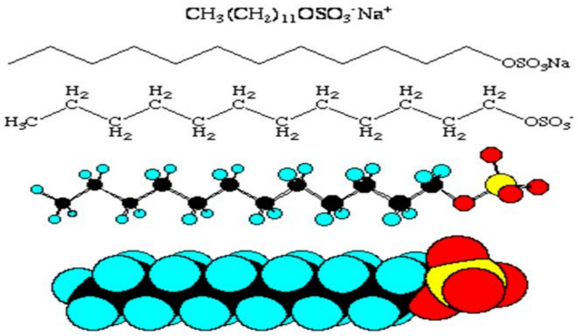
IF the interfacial tension between two liquids is reduced to a sufficiently low value on addition of a surfactant, emulsification will readily take place.

Surfactants

- What is a surfactant?

  *Surf*ace *act*ive *a*ge*nt*





SDS

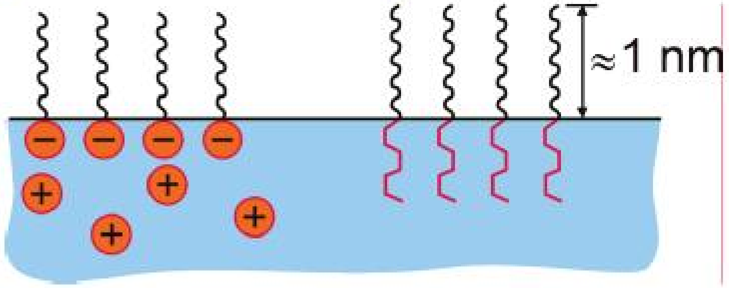
- Headgroup – hydrophilic functional group(s)
- Tail – hydrocarbon or fluorocarbon chain
- Typical headgroups (charged or uncharged)
  - Sulfate: R-SO_3^-
  - Sulfonate: R-SO_4^-
  - Trimethylammonium: R-$N(CH_3)_3^+$
  - Ethylene oxide: R-$(OCH_2CH_2)n$
  - Carboxybetaine: R-$N^+(CH_3)_2(CH_2COO)^-$

Properties of Surfactant Molecules

- Amphiphilic nature of surface active agents causes them to be adsorbed at interfaces, whether these be liquid/gas or liquid/liquid.
- Have a certain affinity for both polar and nonpolar solvents.
- Depending on the number and nature of the polar and nonpolar groups present, the amphiphile may be *hydrophilic, lipophilic* or be reasonably well-balanced between these two extremes.
- Form aggregates in solution called micelles at a specific concentration of surfactant called the *critical micelle concentration (the cmc)*

Types of surfactant

1. Low molecular mass (≈ 200 to 1000)



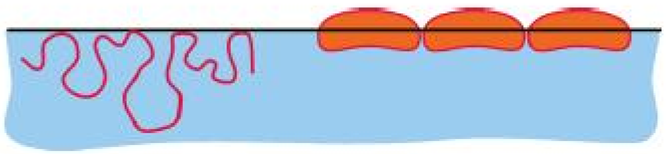
Ionic 

Nonionic 

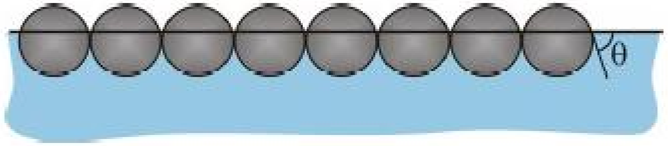
2. Polymeric (including proteins)

Fibrilar

Globular



3. Solid particles



Building Blocks for Surfactant Molecules

- $CH_3(CH_2)_{10}CH_3$: dodecane (insoluble in water)
- $CH_3(CH_2)_{10}CH_2OH$: dodecanol (low solubility, begins to exhibit surface activity)
- $CH_3(CH_2)_{10}COOH$: dodecanoic acid (lauric acid, limited solubility in water)
- $CH_3(CH_2)_{10}COONa$: water soluble, classic soap, reasonably good surfactant
  - → C16: solubility decreases, but surfactant properties improve significantly (foaming, detergency)
  - → Altering balance between the hydrophilic group and hydrophobic group give effective control over the surfactant characteristics.
  - → Drawback of carboxylate soap
    - Very sensitive to their aqueous environment
    - Hard water: Ca^{++}, Mg^{++} (form salts of very low water solubility – precipitate to produce scum deposits)
    - Temperature sensitive: not goof for cold water
    - Acidic environment: form RCOOH
- Synthetic surfactants (detergents)
  - $CH_3(CH_2)_{10}CH_2SO_3H$: soluble in water, but strong acid characteristics
  - $CH_3(CH_2)_{10}CH_2SO_3M$: M(alkalic, organic amines, other basic ingredients) – excellent surfactants

Building Blocks for Surfactant Molecules

- Alkyl polyoxyethen (POE) polyether (Nonionic)

  $C_{11}H_{23}CH_2\text{-}O\text{-}CH_2CH_2(OCH_2CH_2)_nOCH_2CH_2OH$

  n=10: significant solubility in water, good surfactants

  n=5: little solubility in water, not good surfactants

  n=20: highly soluble in water, surfactant quality lost

- Ampholytic

  $CH_3(CH_2)_{10}CH_2Cl + (CH_3)_3N \rightarrow CH_3(CH_2)_{10}CH_2N^+(CH_3)_3Cl^-$ (dodecyltrimethylammoniumchloride)

  water soluble, some surfactant properties

  $CH_3(CH_2)_{10}CH_2Cl + (CH_3)_2N\,(CH_2)_3SO_3H \rightarrow CH_3(CH_2)_{10}CH_2N^+(CH_3)_2(CH_2)_3SO_3^-$

  - manipulate the hydrophilic group and hydrophobic group → many possibilities

Applications of Surfactants

- Surfactants are also widely used in industry due to their ability to lower surface and interfacial tensions and act as wetting agents and detergents
  - Heavy and tertiary oil recovery
  - Ore flotation
  - Dry cleaning
  - Pesticide and herbicide applications
  - Water repellency

- Surfactants are an integral part of everyday life; they are formulated into a wide variety of consumer products
  - Shampoos
  - Dish detergents
  - Laundry detergents
  - Conditioners
  - Fabric softeners
  - Diapers
  - Contact lens cleaners

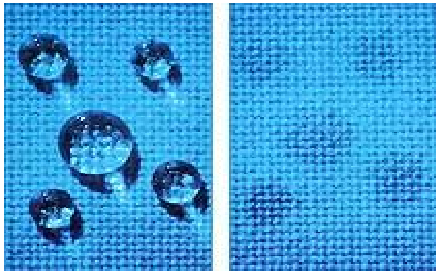
Classification of Surface Active Agents

Functional Classification

According to their pharmaceutical use, surfactants can be divided into the following groups:

- **Wetting agents**
- **Solubilizing agents**
- **Emulsifying agents**
- **Dispersing, Suspending and Deflocculating agents**
- **Foaming and antifoaming agents**
- **Detergents**

Wetting agents



Wetting agent is a surfactant that when dissolved in water, lower the contact angle and aids in displacing the air phase at the surface and replacing it with a liquid phase.

Solids will not be wetted if their critical surface tension is exceeded than the surface tension of the liquid. Thus water with a value of 72 dynes/cm will not wet polyethylene with a critical surface tension of 31 dynes/cm.

Based on this concept we should expect a good wetting agent to be one which reduces the surface tension of a liquid to a value below the solid critical surface tension.

Micellar Solubilization

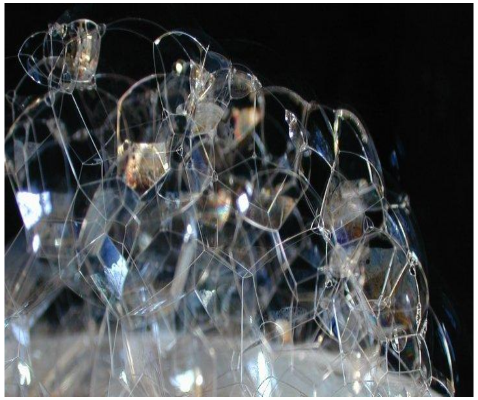
Surfactant solution above the CMC can solubilize otherwise insoluble organic material by incorporating it into the interior of the micelles.

Micelles form around the molecules of the water insoluble compound inside the micelles' cores and bring them into solution in an aqueous medium. This phenomenon is called micellar solubilization.

Solubilization is of practical importance in the formulation of pharmaceutical and other products containing water-insoluble ingredients, detergency, emulsion polymerization and micellar catalysis of organic reations.

As Micellar solubilization depends on the existence of micelles; it does not take place below the CMC. So dissolution begins at the CMC. Above the CMC, the amount solubilized is directly proportional to the surfactant concentration because all surfactant added to the solution in excess of the CMC exists in micellar form, and as the number of micelles increases the extent of solubilization increases .

Foaming and Anti Foaming agents



- *Foams are dispersion of a gas in a liquid (liquid foams as that formed by soaps and detergents) or in a solid (solid foams as sponges).*

- **Foaming agents**

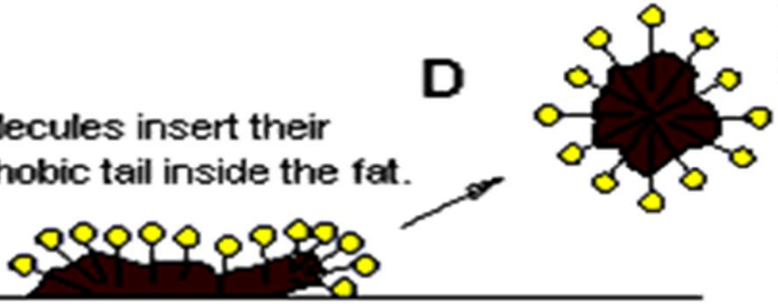
Many Surfactants solutions promote the formation of foams and stabilize them, in pharmacy they are useful in toothpastes compositions.

- **Anti Foaming agents**

They break foams and reduce frothing that may cause problems as in foaming of solubilized liquid preparations. in pharmacy they are useful in aerobic fermentations, steam boilers.

Detergents

- Detergents are surfactants used for removal of dirt.
- Detergency involves:
  - Initial wetting of the dirt and the surface to be cleaned.
  - Deflocculation and suspension, emulsification or solubilization of the dirt particles
  - Finally washing away the dirt.



The molecules insert their hydrophobic tail inside the fat.

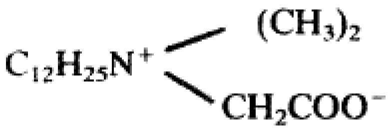
The polar and hydrophilic heads, carry the dirt in the water. The agitation of the fluid make easier the process.

How surfactants remove the dirt

Structural Classification

- **A single surfactant molecule contains one or more hydrophobic portions and one or more hydrophilic groups.**
- **According to the presence of ions in the surfactant molecule they may be classified into:**
  - ☐ **Ionic surfactants**
    - **Anionic surfactants: the surface active part is anion(negative ion)**
      e.g. soaps, sodium lauryl sulfate
    - **Cationic surfactants: the surface active part is cation (positive ion)**
      e.g. quaternary ammonium salts
    - **Ampholytic surfactants: contain both positive and negative ions**
      e.g. dodecyl-B-alanine.
  - ☐ **Non-ionic surfactants:** polyethylene oxide products.

Table 4.2 Surface-active agents

Anionic	
Sodium stearate	$CH_3(CH_2)_{16}COO^-Na^+$
Sodium oleate	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COO^-Na^+$
Sodium dodecyl sulphate	$CH_3(CH_2)_{11}SO_4^-Na^+$
Sodium dodecyl benzene sulphonate	$CH_3(CH_2)_{11}.C_6H_4.SO_3^-Na^+$
Cationic	
Dodecylamine hydrochloride	$CH_3(CH_2)_{11}NH_3^+Cl^-$
Hexadecyltrimethyl ammonium bromide	$CH_3(CH_2)_{15}N(CH_3)_3^+Br^-$
Non-ionic	
Polyethylene oxides	e.g. $CH_3(CH_2)_{11}(O.CH_2.CH_2)_6OH$*
Spans (sorbitan esters)	
Tweens (polyoxyethylene sorbitan esters)	
Ampholytic	
Dodecyl betaine	 $C_{12}H_{25}N^+ \begin{matrix} \nearrow (CH_3)_2 \\ \searrow CH_2COO^- \end{matrix}$

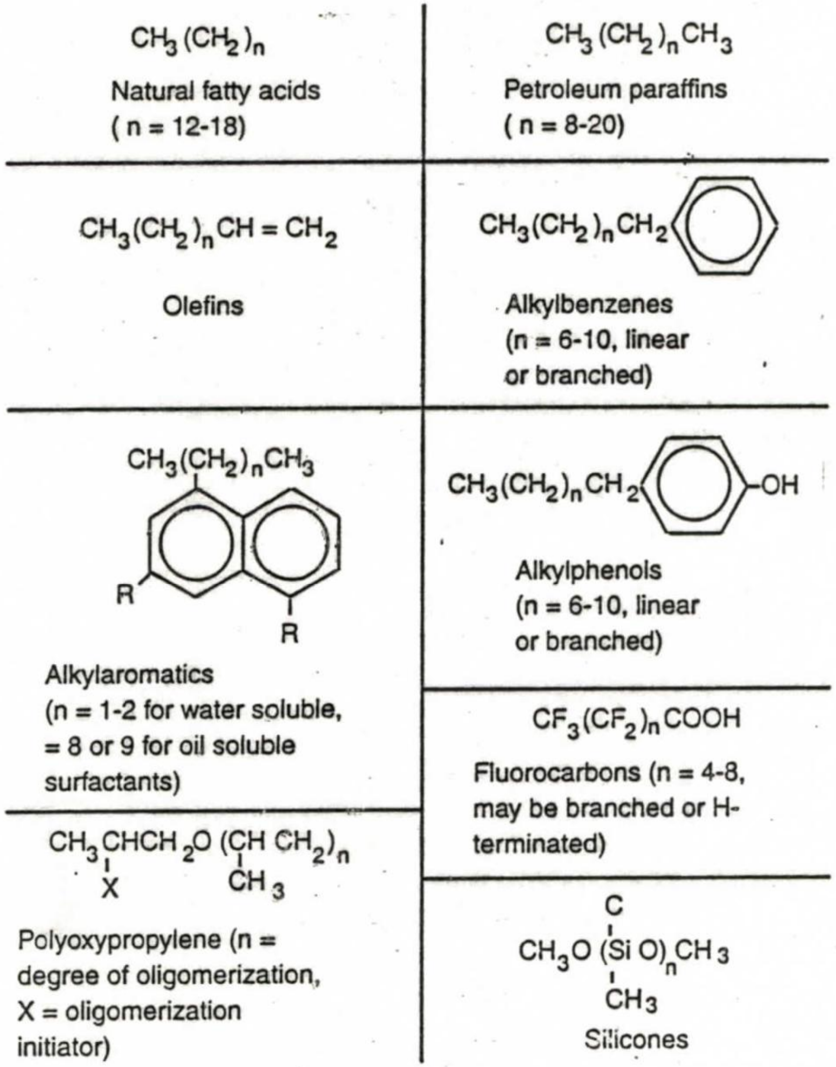
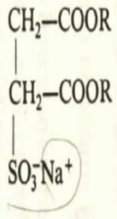
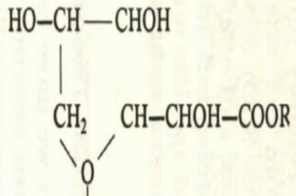
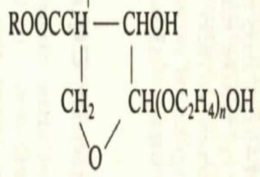
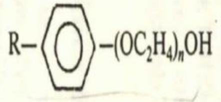
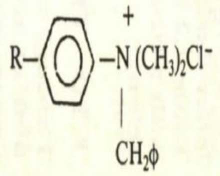


FIGURE 3.4. The most commonly encountered hydrophobic materials used in the commercial manufacture of surfactants.

Table 7.2 Some Families of Commercial Surfactants and Specific Examples from Each

Name of series	General chemical nature	Specific designation ("____") and chemical nature of example	Example
Igepon "____"	Fatty acid amide of methyltaurine	"TN" R = palmityl	$RCON(CH_3)C_2H_4SO_3^- Na^+$
Aerosol "____"	Alkyl ester of sulfosuccinic acid	"OT" R = octyl	 $CH_2{-}COOR$ | $CH_2{-}COOR$ | $SO_3^- Na^+$
Span "____"	Fatty acid esters of anhydrosorbitols	"60" R = stearyl	
Tween "____"	Fatty acid ester and ethylene oxide esters of anhydrosorbitols	"21" n = 4, R = lauryl	
Triton "____"	Ethylene oxide ethers of alkyl benzene	"X-45" n = 5, R = octyl	
Hyamine "____"	Alkylbenzyl dimethyl ammonium salts	"3500" R = C_{12}-C_{16}	

Source: Data from Surfactants, in *Encyclopedia of Chemical Technology*, Vol. 19, Wiley, New York, 1969.

Commonly used surfactants

Chemical Class	Application
1. *Anionic*	
Alkyaryl sulfonates	Detergents, emulsifiers
Fatty alcohol sulfates	Detergents, emulsifiers
Lignosulfonates	Dispersants
Alkali soaps of tall oil	Anionic emulsifiers
Alkali soaps of rosin	Anionic emulsifiers
Dialkylsulfosuccinates	Wetting agents
2. *Cationic*	
Alkyltrimethylammonium chloride	Emulsifier, corrosion, inhibitor, textile softener, antibacterial agent, detergent
3. *Nonionic*	
Alkanolamides	Detergents, foam stabilizers
Glyceryl esters	Emulsifiers
Ethylene-oxide condensates of alkylphenols	Emulsifiers
Ethoxylated alkylphenols	Detergents, wetting agents, emulsifiers, dispersants
Ethoxylated fatty esters	Food emulsifiers (oil in water)
Fatty esters	Food emulsifiers (water in oil)
Polyalkylsuccinimides	Oil-soluble dispersants
Lecithins	Oil-soluble dispersants
Metal soaps	Oil-soluble dispersants

Anionic surfactants

They are the metal salts of long chain fatty acids as lauric acid.
Sodium dodecyl sulfate or Sodium Lauryl Sulfate **is used in toothpaste and ointments**
Triethanolamine dodecyl sulfate **is used in shampoos and other cosmetic preparations.**
Sodium dodecyl benzene sulfonate **is a detergent and has germicidal properties.**
Sodium dialkylsulfosuccinates **are good wetting agents.**

Cationic surfactants

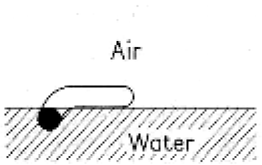
These are chiefly quaternary ammonium compounds.

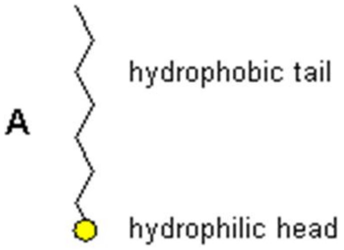
Non-ionic surfactants

They are polyethylene oxide products.
Widely used (Tweens, Spans, Brij and Myrj).
Span 20, 40, 60 or 80: water-insoluble surfactants.
Tween 20, 40. 60 or 80: water-soluble (20 ethylene oxide molecules)

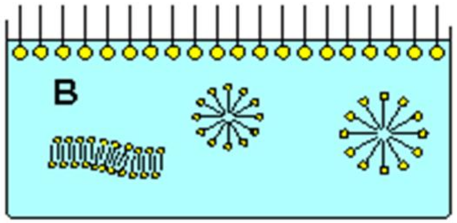
At low surfactant concentrations:

The hydrocarbon chains of surfactant molecules adsorbed in the interface lie nearly flat on the water surface.





scheme of molecule of surfactant



Surfactants arrange themselves on the water surface like a monolayer of molecules, and inside it as micelles and membranes tied by their hydrophobic tail. As the cohesion of these molecules is inferior to that of the molecules of water, the surface tension of water is lowered.

At higher concentrations:

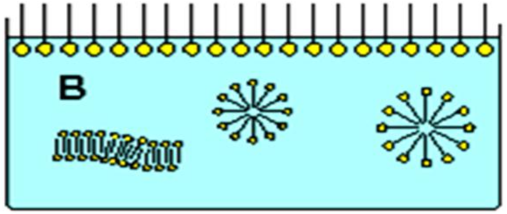
They stand upright because this permits more surfactant molecules to pack into the interfacial monolayer.

As the number of surfactant molecules adsorbed at the water/air interface increased, they tend to cover the water with a layer of hydrocarbon chains. Thus, the water-air interface is gradually transformed into an non polar-air interface. This results in a decrease in the surface tension of water.

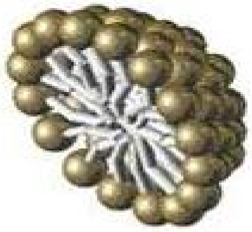
Micelle Formation

When the surfactant molecules adsorbed as a monolayer in the water-air interface have become so closely packed that additional molecules cannot be accommodated with ease, the polar groups pull the hydrocarbon chains partly into the water. At certain concentration the interface and the bulk phase become saturated with monomers. Excess surfactants add will begin to agglomerate in the bulk of the solution forming aggregates called Micelles and the free energy of the system is reduced

The lowest concentration at which micelles first appear is called the critical concentration for micelle formation [CMC]



Surfactants arrange themselves on the water surface like a monolayer of molecules, and inside it as micelles and membranes tied by their hydrophobic tail. As the cohesion of these molecules is inferior to that of the water, the surface tension of water is lowered.



- **At a given concentration, temperature, and salt content, all micelles of a given surfactant usually contain the same number of molecules, i.e. they are usually monodisperse.**
- **For different surfactants in dilute aqueous solutions, this number ranges approximately from 25 to 100 molecules.**
- **The diameters of micelles are approximately between 30 and 80 A^{o}. Because of their ability to form aggregates of colloidal size, surfactants are also called association colloids.**
- **Micelles are not permanent aggregates. They form and disperse continually.**

Surfactant shapes in colloidal solution

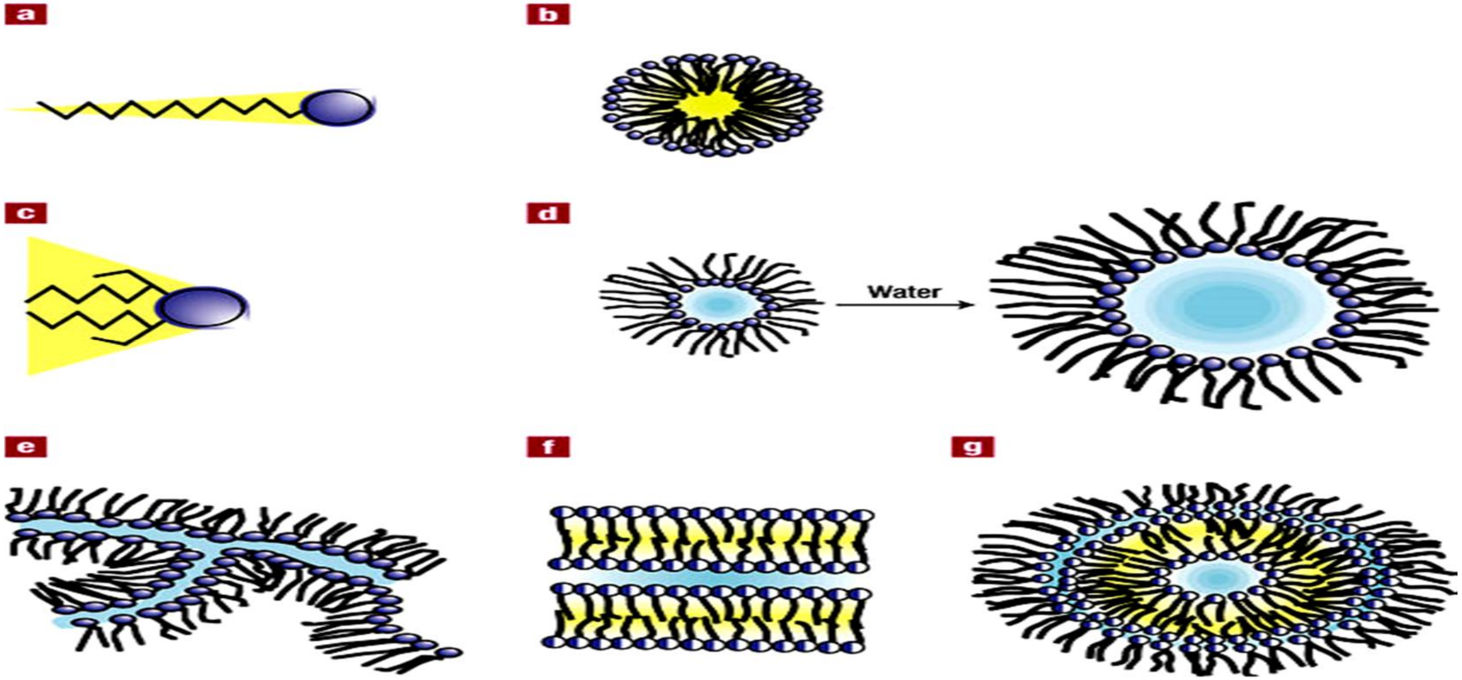
a- Cone-shaped surfactant resulting in b-normal micelles

c- Champagne cork shaped surfactant resulting in d-reverse micelles with control of their size by the water content

e- Interconnected cylinders .

f- Planar lamellar phase .

g- Onion-like lamellar phase.



Normal spherical micelles

In dilute aqueous solutions micelles are approximately spherical.

The polar groups of the surfactants are in the periphery and the hydrocarbon chains are oriented toward the center, forming the core of the micelles

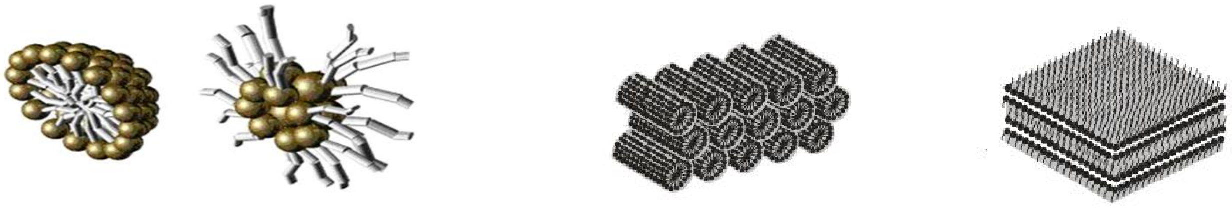
Inverted spherical micelles

In solvents of low polarity or oils micelles are inverted.

The polar groups face inward to form the core of the micelle while the hydrocarbon chains are oriented outward

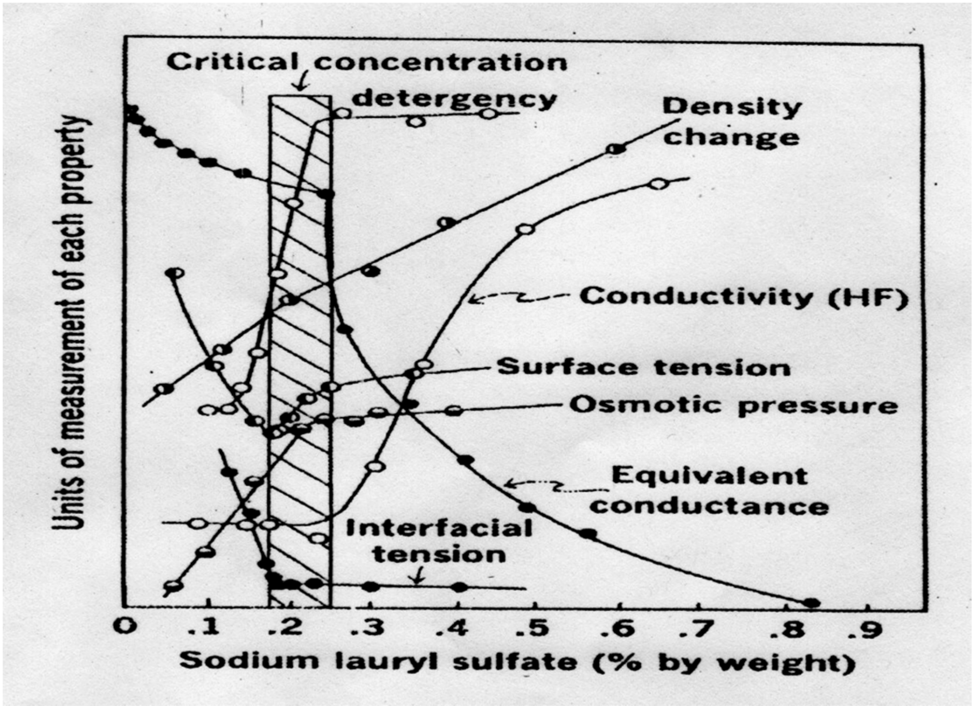
Cylindrical and lamellar micelles

In more concentrated solutions of surfactants, micelles change from spherical either to cylindrical or lamellar phase.



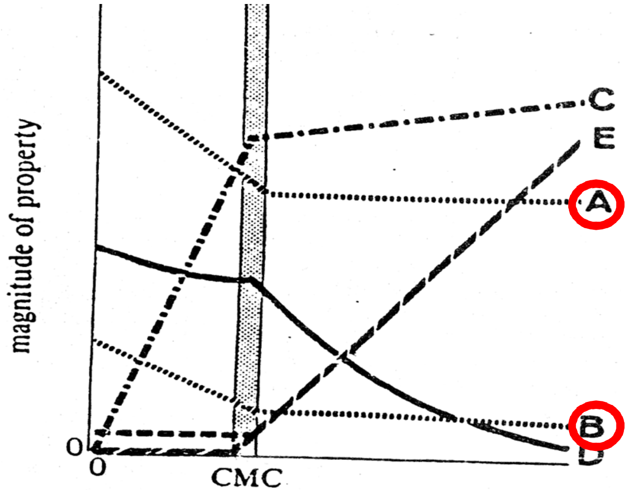
Changes occurred at the CMC

Properties of surfactant Solutions as functions of concentration:



Changes occurred at the CMC

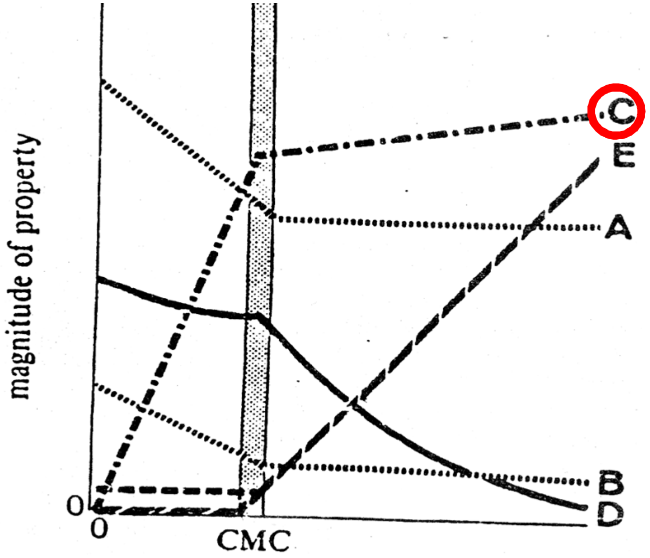
I- A continuous decrease in Surface and interfacial tensions with surfactants concentration until CMC the Surface and interfacial tensions level become constant owing to crowding of surfactant molecules adsorbed at surfaces and interfaces.



A, surface tension
B, interfacial tension
C, osmotic pressure;
D, equivalent conductivity;
E, solubility of compounds with low or zero solubility in water

Changes occurred at the CMC

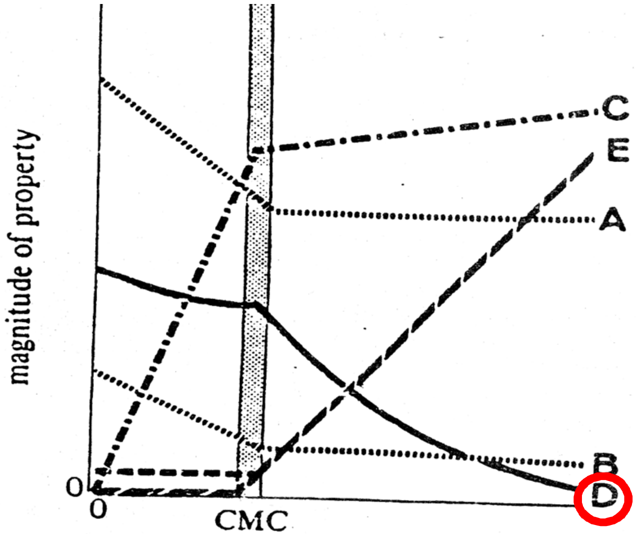
II- The osmotic pressure (and all other colligative properties, lowering of the vapor pressure and of the freezing point), rises much more slowly with increasing surfactant concentration above than it does below the CMC because it depends on the number of dissolved particles.



A, surface tension
B, interfacial tension
C, osmotic pressure
D, equivalent conductivity
E, solubility of compounds with low or zero solubility in water

Changes occurred at the CMC

III- For ionic surfactants, the equivalent conductivity drops sharply above the CMC. Only the counterions of non-associated surfactant molecules can carry current.

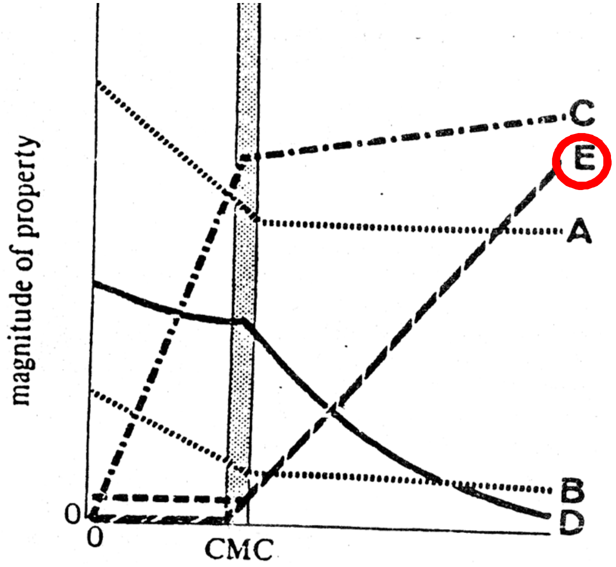


A, surface tension
B, interfacial tension
C, osmotic pressure
D, equivalent conductivity
E, solubility of compounds with
low or zero solubility in water

Changes occurred at the CMC

IV-Solubility of many drugs are increased after CMC.
Other solution properties changing at the CMC: intrinsic viscosity and turbidity increase, while diffusion coefficient decreases

All these properties can be used to determine the CMC.



A, surface tension
B, interfacial tension
C, osmotic pressure
D, equivalent conductivity
E, solubility of compounds with low or zero solubility in water

Factors affecting CMC

For nonionic surfactants

Temperature ↑ CMC ↓

For ionic surfactants

The CMC are higher for ionic than nonionic surfactants.

The charges in the micelle of ionic surfactant are in close, to overcome the resulting repulsion an electric work is required but nonionic surfactants have no electric repulsion to overcome in order to aggregate.

Effect of electrolytes on the CMC of ionic surfactants

The addition of salts to ionic surfactant solutions reduces the electric repulsion between the charged groups and lower CMC values

Effect of Surfactant's structure on CMC

Branched chain systems and double bonds raise CMC

Since the chains must come together inside the micelles

Length of hydrocarbon chain

Increase in chain length of hydrocarbon facilitate the transfer from aqueous phase to micellar form cause decrease in CMC (e.g. Alkyl sulfonates: C8 → 10^{-1}M, C18→10^{-4}M)

- each additional CH_2: halves the CMC

- branch chains: effect ½ that of straight chain

Hydrophilic part of Surfactants

Greater interaction with water will retard micelle formation thus ionized surfactants have higher CMC in polar solvents than nonionic Surfactants.

In polar solvents:

Polarity of Surfactant molecules → CMC ↑

Length of hydrocarbon chain → CMC ↓

In non-polar solvents:

Polarity of Surfactant molecules → CMC ↓

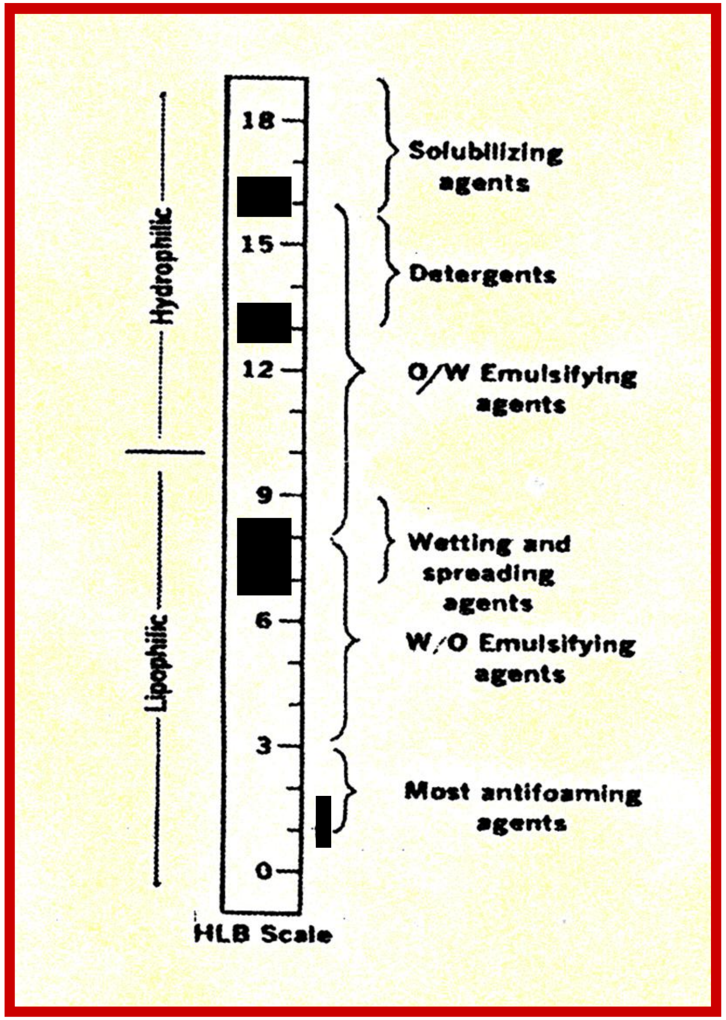
Length of hydrocarbon chain → CMC ↑

Hydrophilic Lipophilic Balance

A scale showing classification of surfactant function on the basis of HLB values of surfactants.

The higher the HLB of a surfactant the more hydrophilic it is.

Example: *<u>Spans</u>* with low HLB are lipophilic. Tweens with high HLB are hydrophilic.



Determination of HLB

- ☐ **Polyhydric Alcohol Fatty Acid Esters (Ex. Glyceryl monostearate)**

$$\boxed{HLB = 20\,(1 - S / A)}$$

***S* = Saponification number of the ester**

***A* = Acid number of the fatty acid**

- ☐ **Surfactants with no Saponification no (Ex. Bees wax and lanolin)**

$$\boxed{HLB = E + P / 5}$$

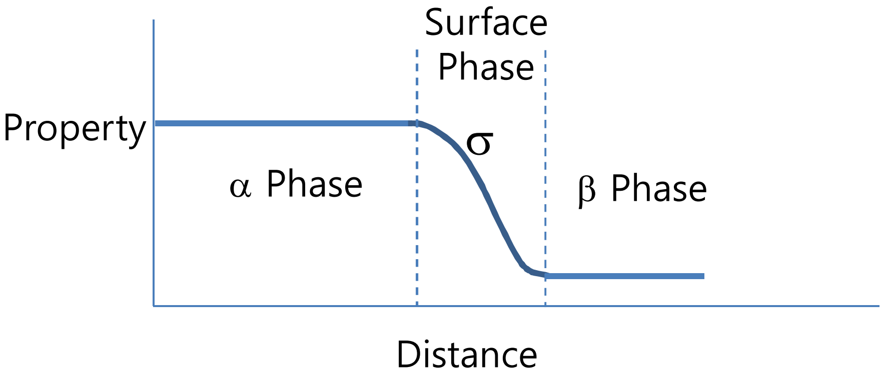
***E* = The percent by weight of ethylene oxide**

***P*=The percent by weight of polyhydric alcohol group in the molecules**

- ☐ **Surfactants with hydrophilic portion have only oxyethylene groups**

$$\boxed{HLB = E / 5}$$

Thermodynamics of Adsorption



1. Guggenheim Approach

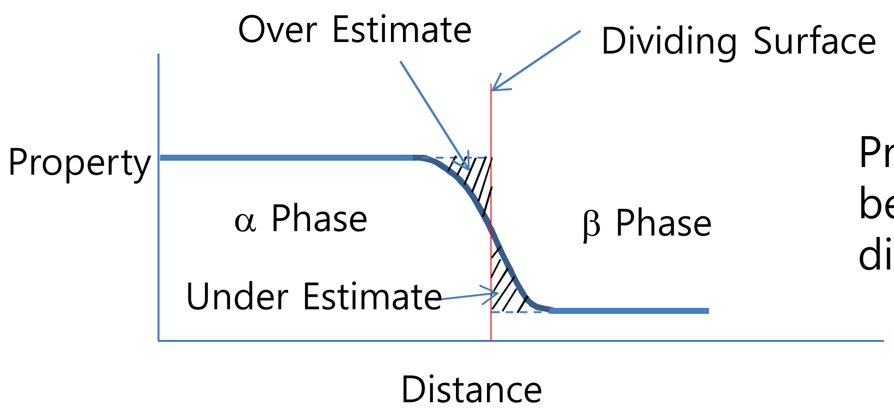
$$dU^{\alpha} = TdS^{\alpha} - PdV^{\alpha} + \sum_{i=1}^{k} \mu_i \, dn_i{}^{\alpha}$$

$$dU^{\beta} = TdS^{\beta} - PdV^{\beta} + \sum_{i=1}^{k} \mu_i \, dn_i{}^{\beta}$$

$$dU^{\sigma} = TdS^{\sigma} - PdV^{\sigma} + \sum_{i=1}^{k} \mu_i \, dn_i{}^{\sigma} + \gamma dA$$

$$\left.\begin{array}{l} dU^{\alpha} \\ dU^{\beta} \\ dU^{\sigma} \end{array}\right\} \quad dU = dU^{\alpha} + dU^{\beta} + dU^{\sigma}$$

2. Gibbs Approach



Properties are assumed to be uniform up to the dividing surface

Surface Excess

$$U = U^{\alpha} + U^{\beta} + U^{S}$$

$$S = S^{\alpha} + S^{\beta} + S^{S}$$

$$V = V^{\alpha} + V^{\beta}\ (V^{S} = 0)$$

$$dU^{S} = TdS^{S} + \sum_{i=1}^{k} \mu_i \, dn_i{}^{S} + \gamma dA$$

$$dG^{S} = -S^{S}dT + \sum_{i=1}^{k} \mu_i \, dn_i{}^{S} + \gamma dA$$

3. Gibbs Adsorption Equation (Isotherm)

$$dU^S = TdS^S + \sum_{i=1}^{k} \mu_i \, d{n_i}^S + \gamma dA$$

$$U^S = TS^S + \sum_{i=1}^{k} \mu_i \, {n_i}^S + \gamma A$$

$$dU^S = TdS^S + S^S dT + \sum_{i=1}^{k} \mu_i \, d{n_i}^S + \sum_{i=1}^{k} {n_i}^S d\mu_i + \gamma dA + Ad\gamma$$

$$0 = S^S dT + \sum_{i=1}^{k} {n_i}^S d\mu_i + Ad\gamma$$

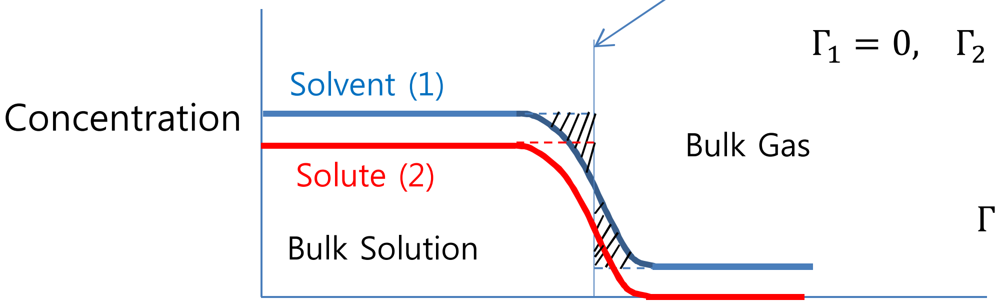
$$d\gamma = -{S_A}^S dT - \sum_{i=1}^{k} \Gamma_i d\mu_i : \text{ Gibbs Adsorption Equation}$$

$${S_A}^S = \frac{S^S}{A} : excess\ entropy, \quad \Gamma_i = \frac{{n_i}^S}{A} : adsorption\ density$$

At const. temp $$d\gamma = -\sum_{i=1}^{k} \Gamma_i d\mu_i : \text{ Gibbs Adsorption Isotherm}$$

Binary System

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2$$



Concentration

Solvent (1)

Solute (2)

Bulk Solution

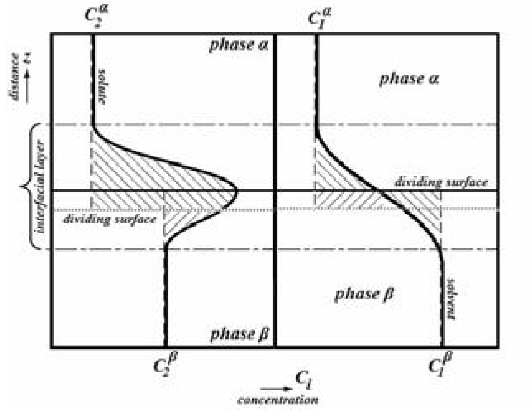
Bulk Gas

Choose location of dividing surface such that

$$\Gamma_1 = 0, \quad \Gamma_2 \neq 0$$

$$d\gamma = -\Gamma'_2 d\mu_2$$

Γ'_2: *adsorption density such that* $\Gamma_1 = 0$



$$\mu_2 = \mu_2{}^0 + RT\ln a_2 \qquad d\mu_2 = RT d\ln a_2$$

$$d\gamma = -\Gamma'_2 RT d\ln a_2 \qquad \Gamma'_2 = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln a_2}\right)_T = -\frac{a_2}{RT}\left(\frac{\partial\gamma}{\partial a_2}\right)_T$$

$$if\ a_2 \cong c_2\ (dilute\ solution) \qquad \Gamma'_2 = -\frac{c_2}{RT}\left(\frac{\partial\gamma}{\partial c_2}\right)_T$$

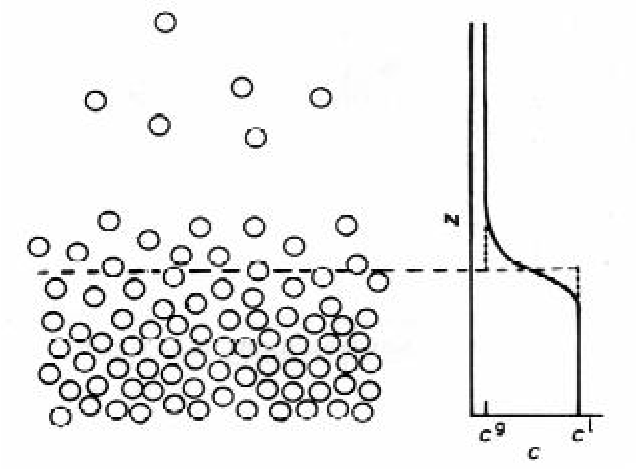
$if\ \dfrac{\partial\gamma}{\partial c_2} < 0,$ $\quad \Gamma'_2 > 0$: excess of solute at the interface (positive adsorption: surfactants)

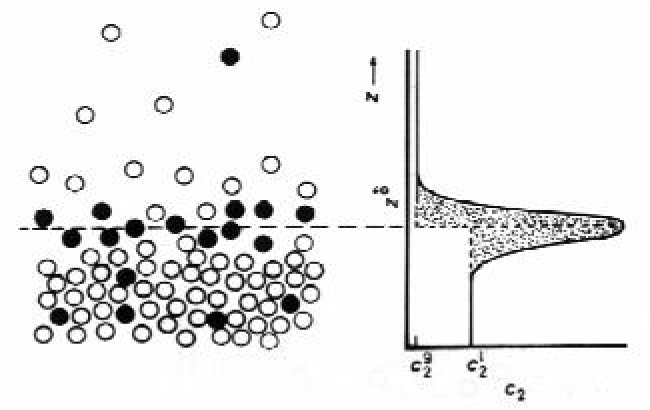
$if\ \dfrac{\partial\gamma}{\partial c_2} > 0,$ $\quad \Gamma'_2 < 0$: deficit of solute at the interface (negative adsorption: inorganic electroylte)

Gibbs adsorption isotherm

@ liquid surface, surface and subphase are in equilibrium:exchange possible

Problem: Location of a surface at a liquid/vapor interface?





Liquid surface: interfacial region a few molecular diameters thick ***(nm)***
Solid surface: interfacial region on a Å scale

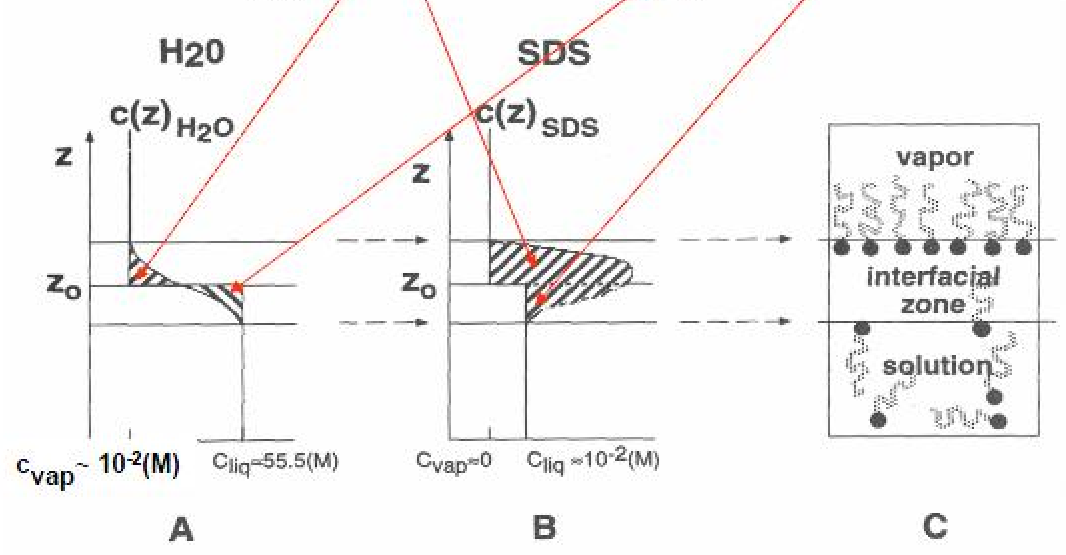
Gibbs adsorption equation

$$\Delta c(z) = c(z) - c_{liq} \qquad \Gamma = \int_{-\infty}^{\infty} \Delta c(z)dz$$

$$\Delta c(z) = c(z) - c_{vap} \qquad \Gamma = \int_{-\infty}^{\infty} (c(z) - c_{vap})dz + \int_{-\infty}^{\infty} (c(z) - c_{liq})dz$$

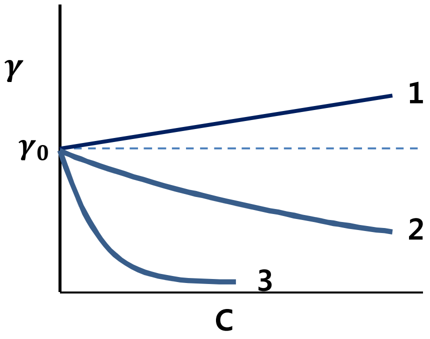
$$\Gamma_1 = \Gamma_{H_2O} = \int_{z_0}^{\infty} (c(z) - c_{H_2O,v})dz + \int_{-\infty}^{z_0} (c(z) - c_{H_2O,liq})dz = 0$$

$$\Gamma_2 = \Gamma_{SDS} = \int_{z_0}^{\infty} (c(z) - c_{SDS,v})dz + \int_{-\infty}^{z_0} (c(z) - c_{SDS,liq})dz$$



$$\frac{d\gamma}{d\mu} = -\Gamma_{SDS}$$

$$\Gamma_{SDS} = -\frac{1}{RT}\frac{d\gamma}{d \ln c_{SDS}}$$



1: simple inorganic electrolytes
2: simple organic solutes
3: amphillic solutes

$$2, 3: \frac{\partial\gamma}{\partial c} < 0, \quad \Gamma'_2 > 0: \quad \text{excess of solute at the interface} \quad \text{(positive adsorption: surfactants)}$$

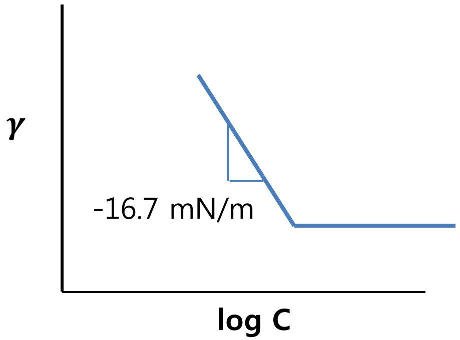
$$1: \frac{\partial\gamma}{\partial c} > 0, \quad \Gamma'_2 < 0: \quad \text{deficit of solute at the interface} \quad \text{(negative adsorption)}$$

2: c→0, $\gamma = \gamma_0 - mc \quad \rightarrow \quad \pi = mc$

$$\frac{d\gamma}{dc} = -m \qquad c = \frac{\pi}{m}$$

$$\Gamma'_2 = -\frac{c_2}{RT}\left(\frac{\partial\gamma}{\partial c_2}\right)_T = \frac{\pi}{RT} \qquad \pi A = n_2{}^S\,RT$$

Carboxylic acid containing less than 12 carbons in the alkyl chain



$$\Gamma'_2 = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial lna_2}\right)_T$$

$$= -\frac{-0.0167}{2.303(8.314)(298)} = 2.93\times10^{-6}\ mol/m^2$$

$$\sigma = -\frac{1\ m^2}{2.93\times10^{-6}(6.02\times10^{23)}} = 0.56\ nm^2$$

Physical state of the monolayers

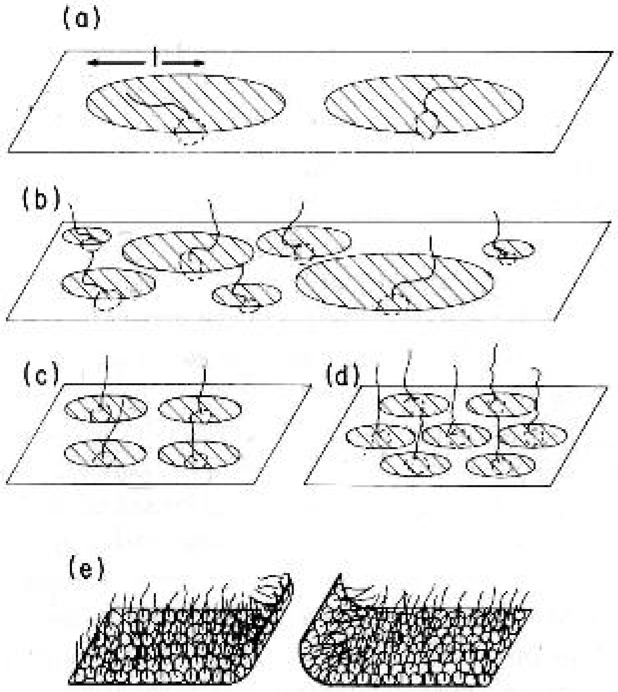


FIGURE 7.6 *Schematic illustration showing by shading the effective area per molecule at various stages of monolayer compression: (a) gaseous state, (b) liquid expanded state, (c) liquid condensed state, and (d) solid state. In (e) the collapse of the film is illustrated.*

Two-dimensional monolayers can exist in different physical states which bear some resemblance to the solid, liquid and gaseous states in three-dimensional matter.

- **Gaseous** or vapor films in which the molecules are separate and move about independently. Large compressibility.
- Liquid films, small compressibility.
- Condensed or solid films in which molecules are closely packed and orientated toward the surface.

Evaporation through monolayers

Monolayer and polymolecular Langmuir - Blodgett (LB) layers

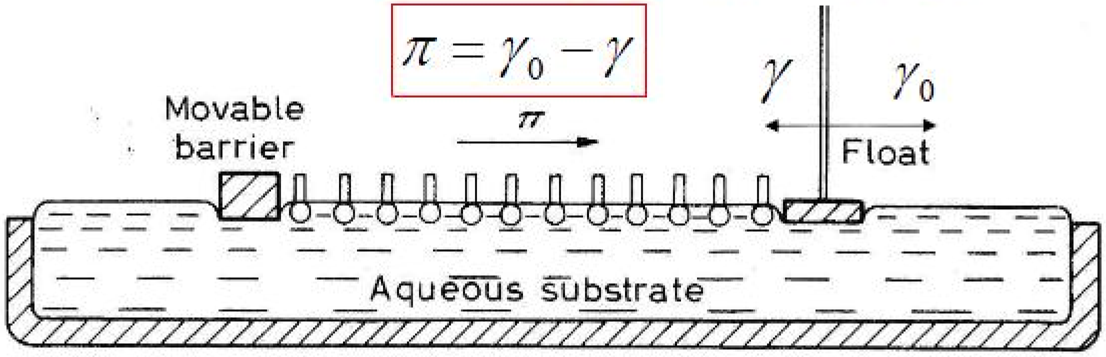


Figure 4.17. The principle of the Langmuir-Adam surface balance

Surface pressure

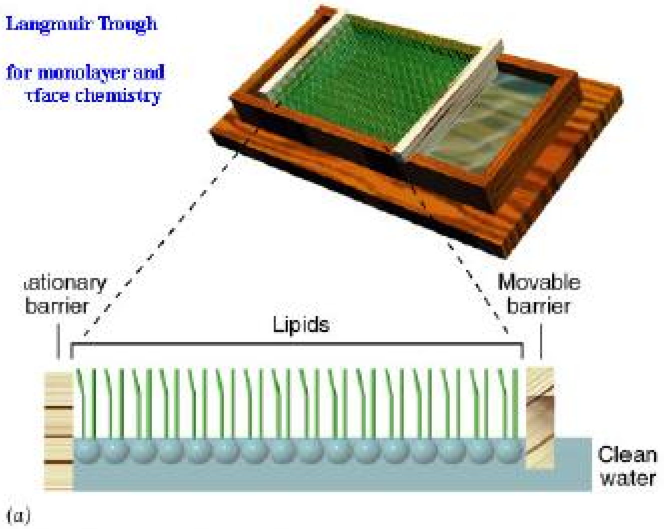
The surface pressure of the film is determined by measuring the force which must be applied to maintain the float at a fixed position on the surface (located optically) and dividing by the length of the float.

Langmuir Films

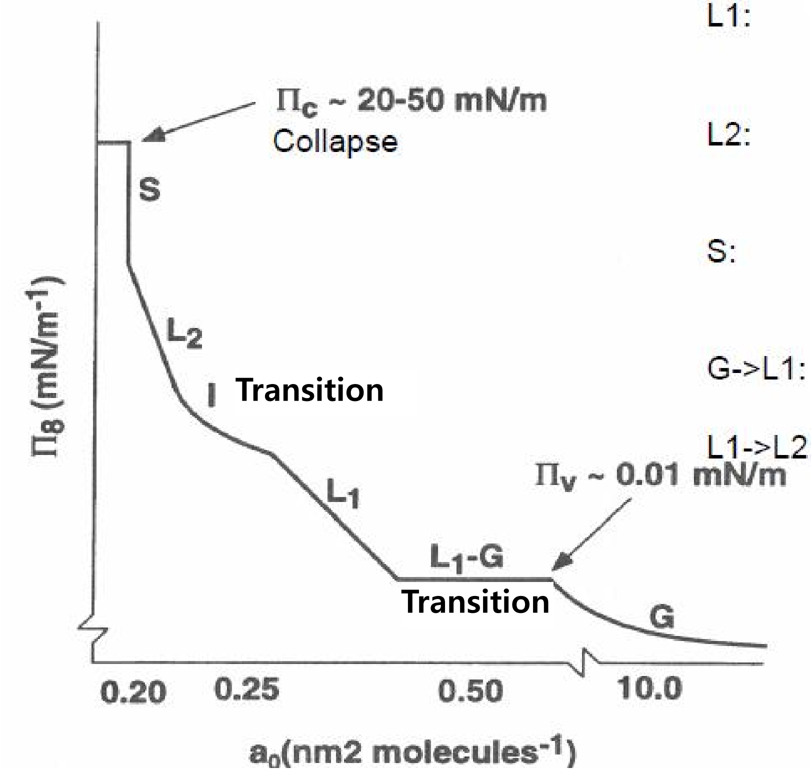
Preparation: dissolve insoluble amphiphiles in a volatile organic solvent and deposit drops of solution onto the air/water interface

S>0 → spreading, evaporation of solvent
→ monolayer of amphiphiles

Pressure is needed to prevent film from spreading $\pi = \gamma_0 - \gamma$



Π-A Isotherm



G:	gas phase
L1:	liquid expanded phase (e.g. saturated unbranched carbon chains: $a_0 \approx 30\text{-}50 Å^2$)
L2:	liquid condensed phase (stronger molecular interactions, lower compressibilty
S:	solid (e.g. alcohols, esters: $a_0 \approx 19\ Å^2$)
G->L1:	typical gas liquid transiton like in 3D
L1->L2:	transition not finally explained.

$$\text{G:}\quad \pi A = nRT \quad R = N_A k$$

$$\pi \frac{A}{N_A n} = \pi\sigma = kT$$

$$\sigma = \pi l^2 \qquad l: lengh\ of\ tail$$

$$\pi = \frac{kT}{\sigma} = \frac{(1.38\times 10^{-23})(298)}{3.14\times (10^{-9})^2} = 1.31\ mN/m$$

L_1: $(\pi - \pi_0)(\sigma - \sigma_0) = kT$
van der Waals equation)

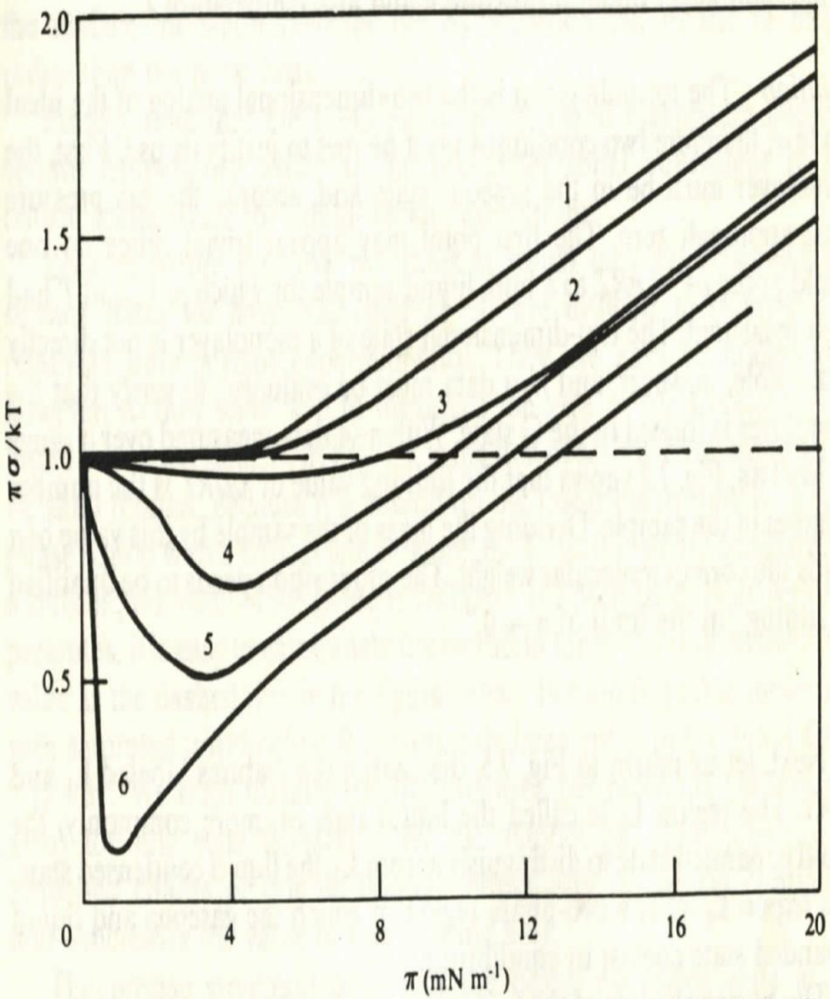


Figure 7.7 Plots of $\pi\sigma/kT$ versus π for *n*-alkyl carboxylic acids: (1) C_4, (2) C_5, (3) C_6, (4) C_8, (5) C_{10}, and (6) C_{12}. [Data from N. K. Adam, *Chem. Rev., 3*:172 (1926).]

Monolayers

- Summary
  - Insoluble monolayers are formed from amphiphiles that are virtually insoluble in water. They can be spread on a water surface from drops of a solution of the amphiphile in a volatile solvent or by spontaneous spreading from crystals or drops of the bulk material. Surface balance is used to manipulate monolayers and is a component of various techniques for measuring monolayers properties.
  - Monolayers exist in a number of phases, must of which can be compared to smectic phases. The major phases are the S, L and G. The hydrophilic part of each molecule anchors the molecule to the water surface and the hydrophobic part is in the air and may be disordered, or organized into hexagonal or rectangular patterns.

Molecular size, shape, conformation and packing can be determined