Lecture Note #3

Liquid surface and liquid-liquid interface

Reading: Shaw, ch. 4

Phenomena at curved surfaces

$\Delta P = P_i - P_0$

1. Pressure difference across a surface

- Liquid drop suspended in vacuum → The equilibrium shape is a sphere

→ Minimization of the surface area for a given volum.

- Can you prove it using the calculus of variation?
- The free energy change dG in contraction from r → r-dr is

$$dG = -\gamma\, 8\pi r\, dr + \Delta P \cdot 4\pi r^2 dr$$

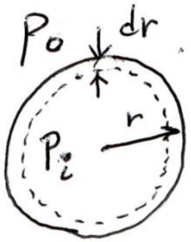
at equilibrium $dG = 0$.

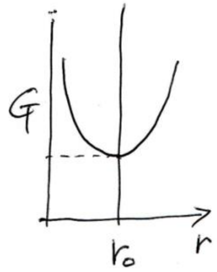
$$\Delta P = \frac{8\pi r\gamma}{4\pi r^2} = \frac{2\gamma}{r} \quad \text{Young-Laplace eq.}$$

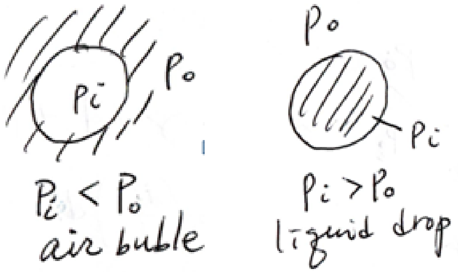
In general, a surface has two principal curvature of radii r_1 and r_2

$$\Delta P = \left(\frac{1}{r_1} + \frac{1}{r_2}\right)\gamma$$

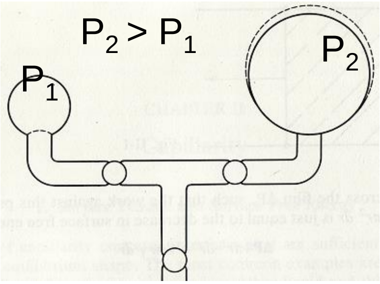
The liquid drop is in a compressed state.







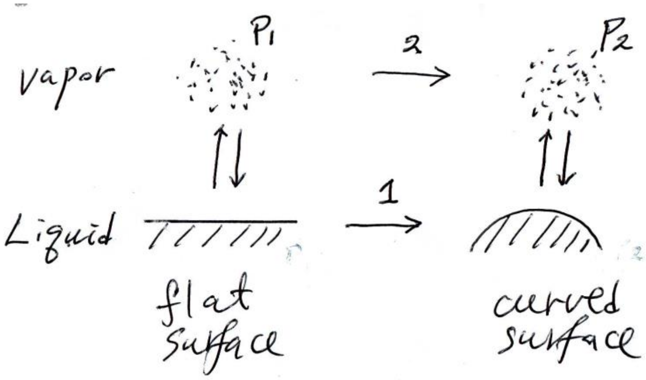
concave convex



The illustration of the equation of Young-Laplace

2. Equilibrium vapor pressure of a liquid drop

A Liquid drop is in a compressed state
→ The inner pressure is higher than that of liquid with a flat surface by ΔP
→ in a higher free energy state → higher vapor pressure.



Chemical potential change in the processes 1 and 2

$$\mu_\ell^{(c)} - \mu_\ell^{(f)} = -\int V\,dp \sim -V_m \Delta P$$

$$\mu_g^{(c)} - \mu_\ell^{(f)} = RT\ln(P_2/P_1)$$

Where V_m is the molar volume of the liquid, which is assumed to be constant.
The two quantities should be the same, and therefore

$$V_m \Delta P = RT\ln(P_2/P_1) \quad \text{or}$$

$$\frac{2V_m\gamma}{r} = RT\ln(P_2/P_1)$$

$$P_2/P_1 = \exp\left[\frac{2V_m\gamma}{rRT}\right]$$

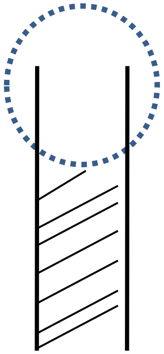
If $r = \infty$, $P_1 = P_2$
For finite r $P_2 > P_1$
For H_2O (γ = 72.8 mN/m) at 300 K
r = 1000 Å → P_2/P_1 = 1.01
r = 100 Å → P_2/P_1 = 101
r = 10 Å → P_2/P_1 = 3.0

Related concepts

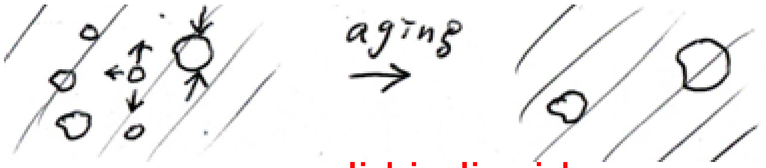
- Size-dependent solubility

  The same concept can be equally applied to the solubility of a particle $c_2/c_1 = \exp(-2V_m \gamma / rRT)$, where c is the concentration in the solution.

- Capillary condensation in porous materials



Oswald ripening



solid in liquid

desolution ↔ deposition process is in a dynamic equilibrium
to maintain a constant saturation solubility.

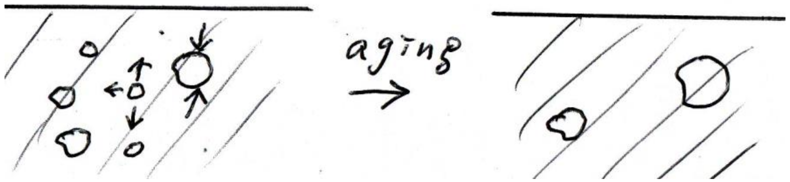
small particle → high solubility and large particle → low solubility

Large particles grow at the expense of the smaller particles → aging

minimize the total surface area → the way to reach a G_{min},
an equilibrium state

AgI sol → highly insoluble → little tendency of ripening (slow kinetics)
$CaCO_3$ sol → highly soluble → strong tendency of ripening (fast kinetics)

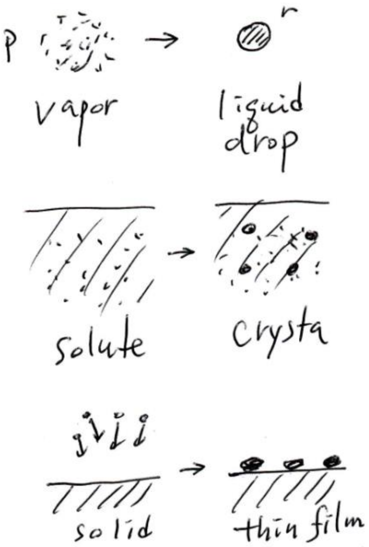
Sintering



solid in (on) solid

3. Formation of a new phase : nucleation and crystal growth

vapor → liquid drop
solute in a liquid → crystal



- In the initial stage of condensation a liquid drop of radius r is formed from a supersaturates vapor.
- Small drop has a high vapor pressure → it tends to reevaporate →
- Therefore, only droplets of a radius greater than a crital radius r_c (embryo) survive and grow.
- This process is called nucleation and the neuclei grow in time.

Consider the free energy change in nucleation of a droplet from a vapor.

nA (gas,P) → A_n (small liquid drop, r)

$$\Delta G = -nkT \ln P/P_0 + 4\pi r^2 \cdot \gamma$$

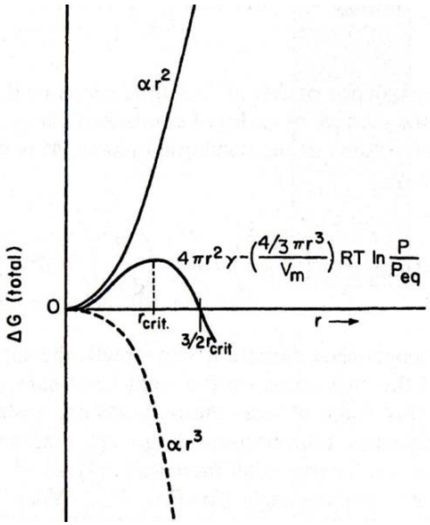
$$= -\frac{4}{3}\pi r^3 \frac{\rho}{M} \ln P/P_0 + 4\pi r^2 \gamma$$

$$d(\Delta G)/dr = 0 \quad \text{at} \quad r = r_c$$

$$r_c = 2\gamma V_m / RT \ln(P/P_0)$$

M= molular weight, ρ = density
P_0 = equilibtitm vapor pressure
P/P_0 = degree of superstuation

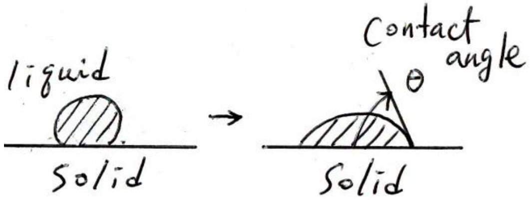
This means there is always a free energy barrier of
$\Delta G_m = 16\,\pi\,\gamma^3\,V_m / 3\,\{RT \ln(P/P_0)\}^2$,
which is overcome by thermal fluctuation.



* Related concepts
artificial raining: spraying dry ice particle in the damp air
seeding in crystallization: adding a ctrstal seeds in a supersaturated solution

4. Capillary rise and depression

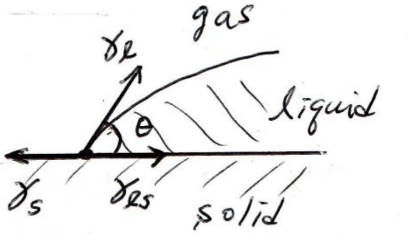
- Wetting



$\theta = 0^o$:complete wetting
$\theta = 180^o$:complete dewetting

- Wetting occurs to minimize the total free energy which includes the surface and interfacial free energies.

- Force balance at the interface



$$\gamma_l \cos\theta + \gamma_{ls} = \gamma_s$$

- Criteria for wetting
  When the interface area is increased by dA,

$$dG = \gamma_{ls}\, dA + \gamma_l \cos\theta\, dA - \gamma_s\, dA$$
$$= (\gamma_{ls} + \gamma_l \cos\theta - \gamma_s)\, dA = x\, dA$$

If $x < 0$ → wetting occurs, and
If $x > 0$ → dewetting occurs.

There is a certain contact angle for which $x = 0$: equilibrium contact angle

Capillary rise

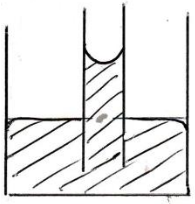
- Force balance at the top of the miniscus

Total wetting force = gravitational force of the water column

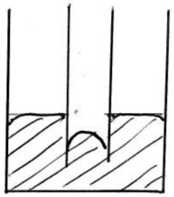
$$2\pi\, r\, \gamma \cos\theta = (\rho - \rho_0)(\pi r^2 h)\, g = \Delta\rho\, (\pi r^2 h)\, g\ ,$$

ρ = deisity of the liquid
ρ_0 = deisity of the air

$$h = 2\gamma \cos\theta / \Delta\rho\, g\, r$$



capillary rise



capillary depression

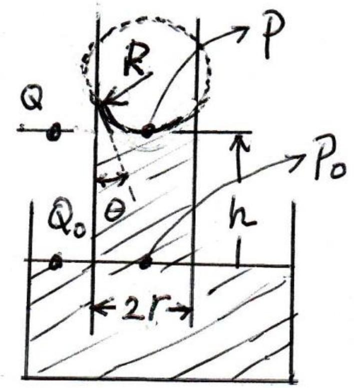
Another view

pressure difference between the points Q and Q_0 : $\Delta P = \rho_0\, g\, h$
pressure difference between the points P and P_0 : $\Delta P = -\,2\gamma/R + \rho\, g\, h$

The two ΔP ‘s should be the same. $r = R\cos\theta$

$$2\gamma/R = \Delta\rho\, g\, h \rightarrow h = 2\gamma\cos\theta / \Delta\rho\, g\, r$$

More accurately, $h' = h + r/3$



Interfacial tension

- Force /unit surface area for a pure liquid = γ
- Force /unit interface area at a liquid-liquid interface/unit length = γ_i
- The total unbalanced force acting on the molecules at the interface

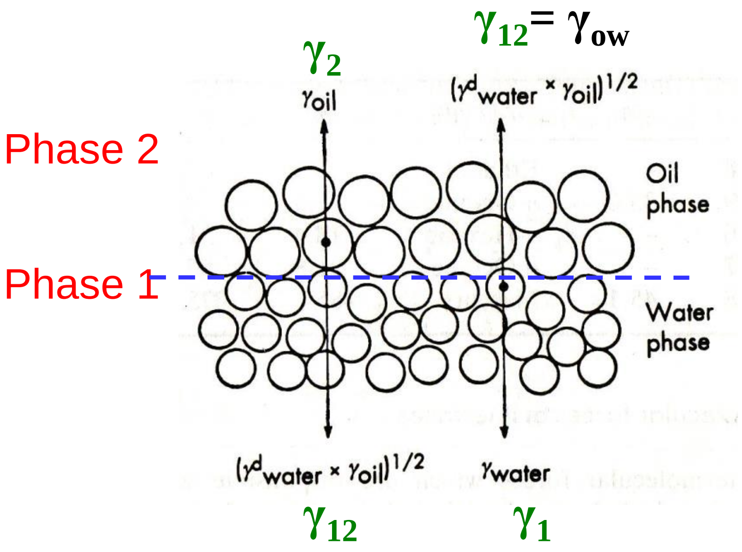
$$\gamma_i = (\gamma_1 - \gamma_{12}) - (\gamma_2 + \gamma_{21}) = \gamma_1 + \gamma_2 - 2\gamma_{12},$$

where $\gamma_{12} = \gamma_{21}$ **(action-reaction)**

γ_i = **free energy per unit interfacial area**

If 1 and 2 are the same materials, $\gamma_i = 0$

- **Consider the case where 2 surfaces are brought from infinity to contact**



Additivity of intermolecular force

$$\gamma_W = \gamma_W^d + \gamma_W^h$$

$$\gamma_{Hg} = \gamma_{Hg}^d + \gamma_{Hg}^m$$

$$\gamma_{OW} = \gamma_O^d + (\gamma_W^d + \gamma_W^h) - 2 \times (\gamma_W^d \times \gamma_O^d)^{1/2}$$

Ex: n-hexane-water interface

$$51.1 = 18.4 + 72.8 - 2 \times (\gamma_W^d \times 18.4)^{1/2}$$

$$\gamma_W^d = 21.8 \text{ mNm}^{-1}$$

$$\gamma_W^h = 72.8 - 21.8 = 51.0 \text{ mNm}^{-1}$$

Table 4.1 Surface tensions and interfacial tensions against water for liquids at 20°C (in mN m^{-1})

Liquid	γ_0	γ_i	*Liquid*	γ_0	γ_i
Water	72.8	–	Ethanol	22.3	–
Benzene	28.9	35.0	*n*-Octanol	27.5	8.5
Acetic acid	27.6	–	*n*-Hexane	18.4	51.1
Acetone	23.7	–	*n*-Octane	21.8	50.8
CCl_4	26.8	45.1	Mercury	485	375

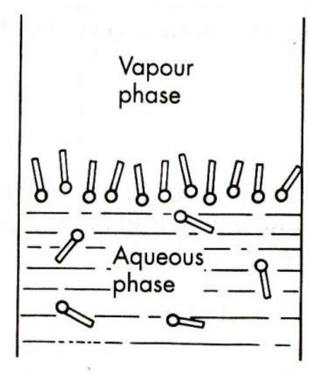
Surface tension of 2-component systems

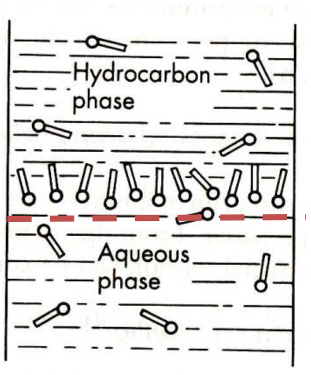
Surface activity

$$\gamma = \gamma_0 - \pi$$

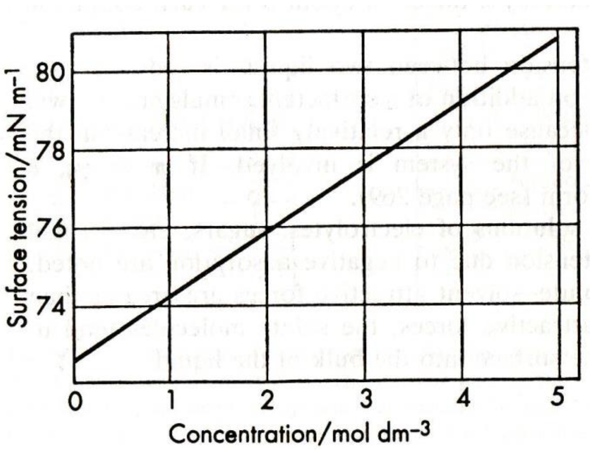
π : surface pressure(expanding pressure)
Surface active agent, surfactant

Adsorption and orientation at interfaces

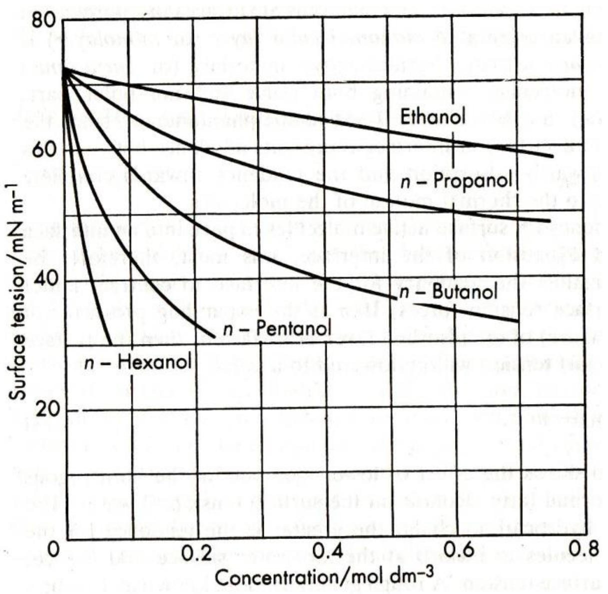




NaCl solution



Alcohol in water



Thermodynamics of surface (or interface)

- The surface tension γ of a pure solvent changes when a solute is added.
- $\Delta\gamma$ $(= \gamma - \gamma_0)$ depends on the concentration c of the solute.
- Thermodynamics can tell the functional relation $\Delta\gamma(c)$.
- The thermodynamic equations for a bulk need to be modified when applied for a surface.

$dU = dq + dw = TdS - P\,dV$ for single-component bulk

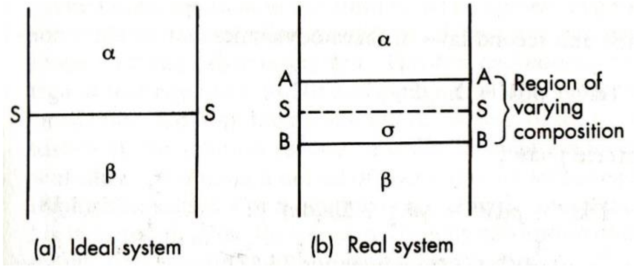
$dU = dq + dw = TdS - P\,dV + \Sigma\, \mu_i n_i$ for multi-component bulk

$U = TS - PV + \Sigma\, \mu_i n_i$ integration at constant T,P, and μ_i

$$dU = SdT - VdP + \Sigma\, n_i d\mu_i = 0$$

Gibbs dividing surface (interface)

- The interface of a real system is blurred.
- The system is considered consisting of
  α phase + βphase + σ plane (ideal abrupt interface)
- The choice of the locus of the σ plane is arbitrarily.



(a) Ideal system (b) Real system

$dU^\sigma = dq + dw = TdS^\sigma - P\,dV^\sigma + \gamma\, dA + \Sigma\, \mu dn_i^\sigma$; surface, multi-component

$U^\sigma = q + w = TS^\sigma - P\,V^\sigma + \gamma\, A + \Sigma\, \mu n_i^\sigma$

$$dU^\sigma = S^\sigma\, dT - V^\sigma\, dP + A\, d\gamma + \Sigma\, n_i^\sigma d\mu_i = 0$$

Gibs-Duhem equation (extended to include the surface)

- Thermodynamic description of mixtures

5.1 Partial molar quantities

a) Partial molar volume

$V_J \equiv (\partial V/ \partial n_J)_{p,T,n'}$ (1)

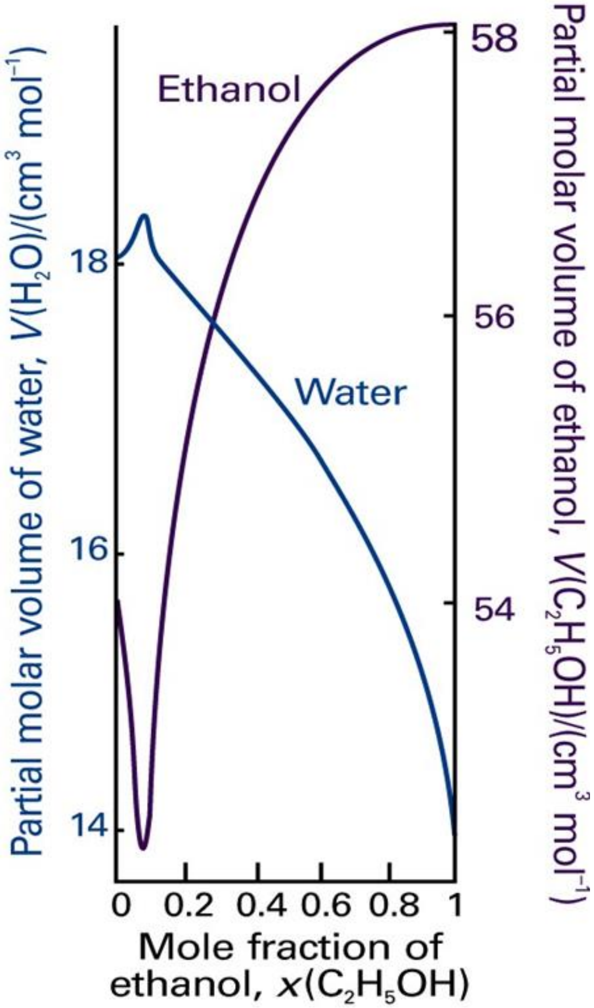
Volume change per 1 mole of J^th species added to a large volume of the mixture.

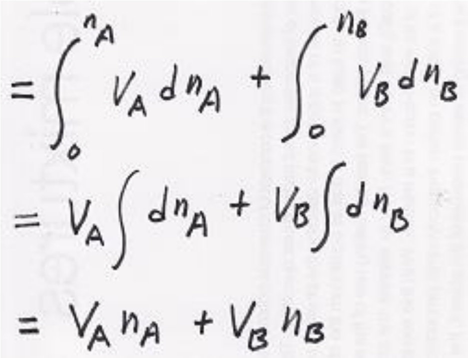
For a binary mixture A+ B,

$$dV = (\partial V/ \partial n_A)_{p,T,nB}\, dn_A + (\partial V/ \partial n_B)_{p,T,nA}\, dn_B$$
$$= V_A\, dn_A + V_B\, dn_B \qquad (2)$$

V_A and V_B are the functions of the composition.

Integrating the eq. (2) keeping the composition constant (see the next page)



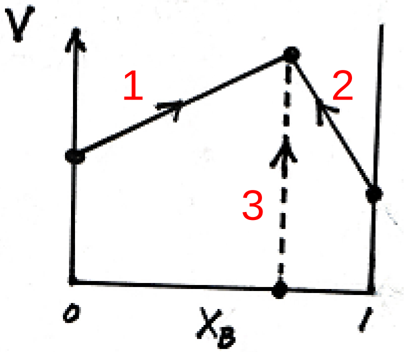
V


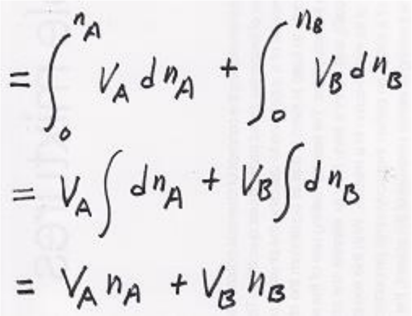
$$V = \int_0^{n_A} V_A\, dn_A + \int_0^{n_B} V_B\, dn_B$$
$$= V_A \int dn_A + V_B \int dn_B$$
$$= V_A n_A + V_B n_B$$

- Consider 3 different ways of mixing two liquids:
  $A\ (n_A) + B\ (n_B) \rightarrow$ n moles of a uniform mixture

- The final volume of the mixture is the same independently of the path→ V is a state function.

- Path 3 corresponds to keeping the composition constant (V_A and V_B constant) in the integration.

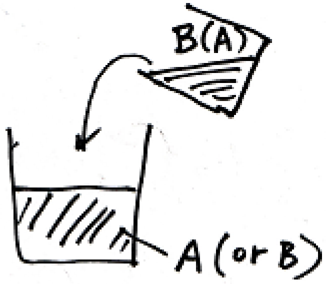




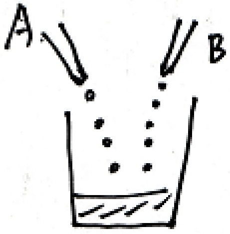
$$V = \int_0^{n_A} V_A\, dn_A + \int_0^{n_B} V_B\, dn_B = V_A \int dn_A + V_B \int dn_B = V_A n_A + V_B n_B$$

- $\boxed{V = V_A n_A + V_B n_B}$
- V_A and V_B are **state functions.**
- $dV = V_A\, dn_A + V_B\, dn_B$
- In general (assuming V_A, V_B are independent of the composition),

  $dV = (V_A\, dn_A + V_B\, dn_B) + (n_A\, dV_A + n_B\, dV_B)$
- $\boxed{n_A\, dV_A + n_B\, dV_B = 0}$ $\rightarrow$ $dV_A = -(n_B / n_A)\, dV_B$
- dV_A and dV_B are **not independent** of each other.



Case 1 or 2



Case 3

Why are V_A and V_B the functions of composition?

- V_A and V_B depend on the intermolecular interactions A-A, A-B, and B-B
- If $V(A\text{-}B) < V(A\text{-}A)$ and $V(B\text{-}B)$, V decreases when B(or A) is added to A(or B).

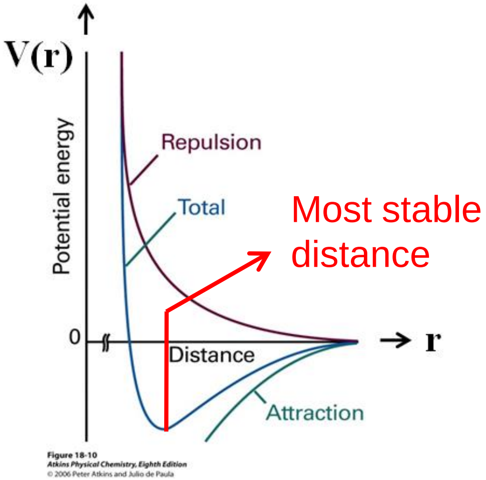


Figure 18-10
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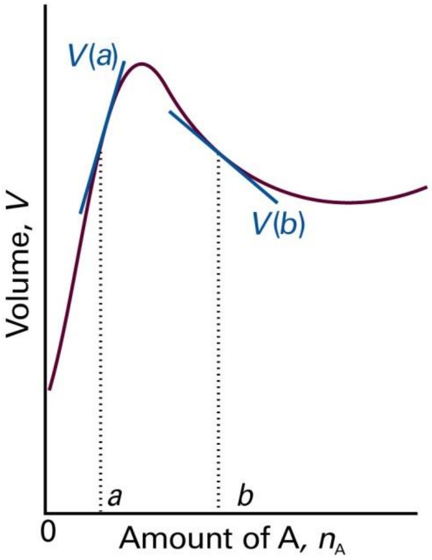
Relation between V_A and V_B

- From $n_A\, dV_A + n_B\, dV_B = 0$, $X_A\, dV_A + X_B\, dV_B = 0$
- Dividing by dX_A, one gets $X_A\, (dV_A /dX_A) + X_B\, (dV_B /dX_A) = 0.$

- The slope of the V_A-X_A and V_B -X_B curves (Fig. 5.1) are inter-related.

- Experimental method of measuring V_A (or V_B)

- Measure V upon adding n_A mole of A into a large amount of B (Fig.5-2) →The slope is the partial molar volume of A at a given mole fraction X_A.



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b) Partial molar Gibbs energy

- $\mu_J \equiv (\partial G/\partial n_J)_{p,T,n'}$ (3)
  $G = \mu_A n_A + \mu_B n_B$ (4)
  $dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B$

- At constant T and P,
  $dG = \mu_A dn_A + \mu_B dn_B$ (5)

In general (assuming μ_A, μ_B are independent of the composition)
$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$ (6)

(6)- (5),

- $\boxed{n_A d\mu_A + n_B d\mu_B = 0}$: Gibbs-Duhem equation

- $d\mu_A$ and $d\mu_B$ are not independent → When a small amount of material A(or B) is added to a binary system, the change in μ_A and μ_B are not independent.

- For a multi-component system, $\sum \mu_J dn_J = 0$

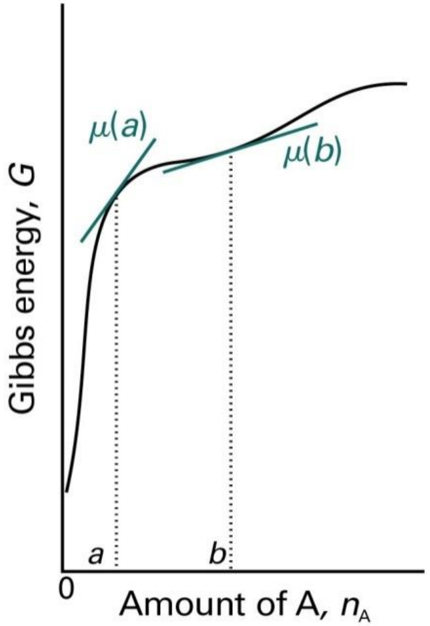

Figure 5-4
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Using the Gibbs-Duhem equation (text example 5.1)

- $\underline{K_2SO_4(s)}$ + $\underline{H_2O}$ → $K_2SO_4(aq)$: binary system

  B A

- Given that V_B is experimentally determined as a function of the molality x (= b/b°);
  $V_B = 32.28 + 18.216\ x^{1/2}$,
  where b = moles # of K_2SO_4 per 1 kg water (molality)
- Find the expression for $V_A(x)$ with $V_A^* = 18.08\ cm^3/mol$ (pure water)

- Solution

  $n_A\, dV_A + n_B\, dV_B = 0$; Gibbs-Duhem equation

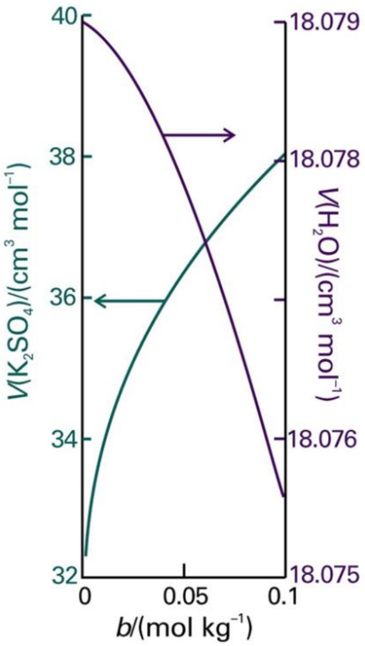
  $dV_A = -\,(n_B / n_A)\, dV_B$

  $n_B / n_A = (b/b^o) / [1000\ g / M_A\ (g/mol)] = 0.018\ x$

  $V_A = V_A^* - \int dV_B = V_A^* - 9.108 \int (n_B / n_A)\ x^{1/2}\, dx$

  $= V_A^* + (2/3)\ (0.018) \int (1/2)\ (0.01821)\ x^{3/2}$

  $V_A\ (cm^3/mol) = 18.079 + 0.1094\ x^{3/2}$



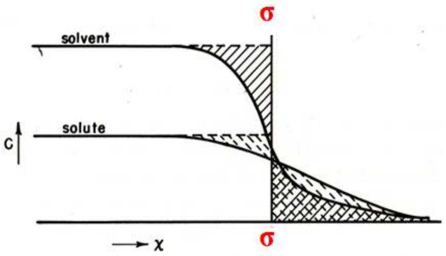
Gibbs adsorption equation

- In general, the concentration profile of solute is different from that of solvent.
- $dU^\sigma = S^\sigma\, dT - V^\sigma\, dP + A\, d\gamma + \Sigma\, n_i^\sigma d\mu_i = 0$
- $\mathbf{A\, d\gamma + \Sigma\, n_i^\sigma d\mu_i = 0}$ at constant T and P
- $\mathbf{n_i^{total} = n_i^\alpha + n_i^\beta + n_i^\sigma}$, where n is the number of molecules (solvent or solute).→ Material conservation

  $\Gamma_i \equiv \mathbf{n_i^\sigma}/A$: surface excess
- $\mathbf{A\, d\gamma + \Sigma\, n_i^\sigma d\mu_i = 0}$ and $\mathbf{d\gamma = - \Sigma\, (n_i^\sigma/A) d\mu_i = - \Sigma\, \Gamma_i\, d\mu_i}$
- For a binary system, solvent (phase1) + solute (phase 2),

  $\mathbf{d\gamma = - (\Gamma_1\, d\mu_1 + \Gamma_2\, d\mu_2)}$
- The position of the σ plane is conveniently taken so that $\mathbf{\Gamma_1 = 0}$ for the solvent.
- Then, $\mathbf{d\gamma = - \Gamma_2\, d\mu_2}$
- $\mathbf{\mu_2 = \mu_2{}^0 + RT \ln a_2}$ For a dilute solution, $a_2 \sim c_2$
- $\mathbf{d\mu_2 = - RT\, (dc_2 / c_2)}$

  $\boxed{\Gamma_2 = - c_2 / RT\, (d\gamma / dc_2)}$: Gibbs adsorption equation

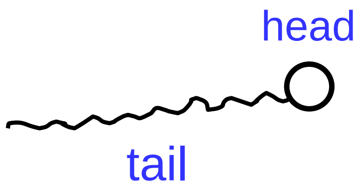


concentration profile along the x direction (⊥σ)

- $\mathbf{\Gamma_2 > 0}$ (+ adsorption): accumulation of solute at the surface (interface).
  Namely, the solute likes to be at the surface (interface).
- $\mathbf{\Gamma_2 < 0}$ (- adsorption): depletion of solute at the surface (interface).
  The solute tends to avoid the surface (interface).
- If $\mathbf{\Gamma_2 > 0}$, i.e., $\mathbf{d\gamma / dc_2 < 0}$, γ decreases with increasing solute concentration.
- Surfactant molecules which causes a large $\Delta\gamma < 0$ strongly positively adsorbs at surface (interface)

Surfactant (surface active agent)

- Molecules which drastically reduces the γ of water when added.
- Typically consists of hydrophobic hydrocarbon chain (tail) and hydrophilic group (head) such as -OH, -COOH, -SO_3H, -NH_2 etc.
- Surfactants are used in many important industrial applications.



Classification of surfactant

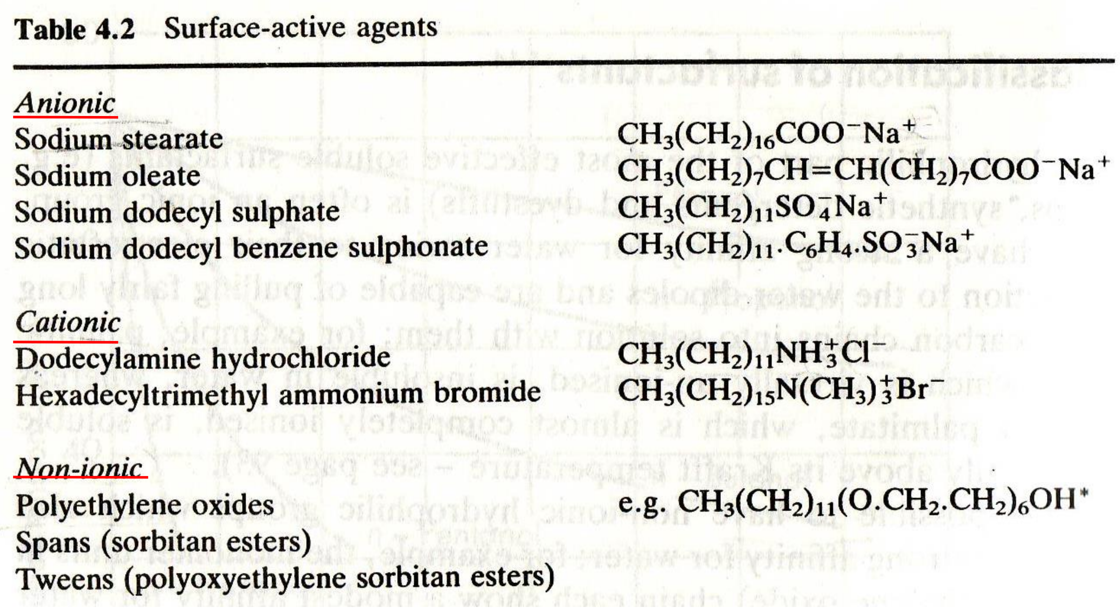
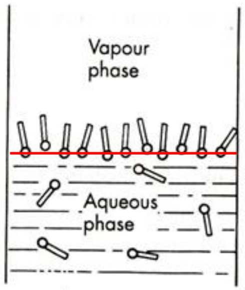


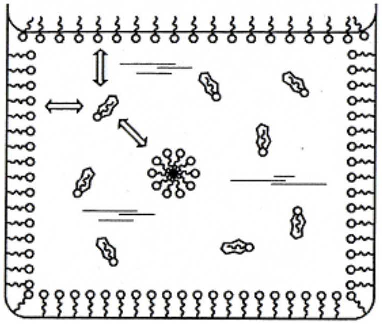
Table 4.2 Surface-active agents

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)	

Self-assembly of surfactant: Micelle formation



- When added in water, surfactant molecules strongly positively adsorb at the surface.
- Surfactant molecules in bulk water is thermodynamically unstable, so the bulk concentration is very small.
- The solubility of surfactants in water, especially the ones with a long alkyl chain, is very low.
- Above a certain temperature, Kraft Temperature T_K, the solubility increases rapidly because of micelle formation.
- Isolated surfactant molecules spontaneously form a stable aggregate
- (micelle) above a certain concentration, critical micelle concentration(CMC)
- Micelle formation occurs sharply at CMC like a phase transition.



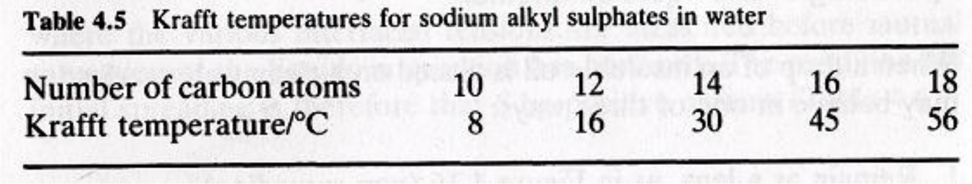
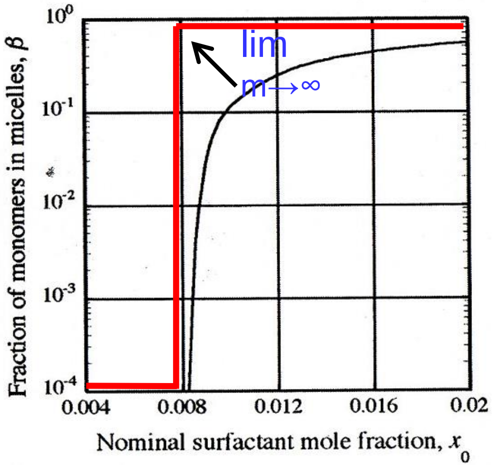


Table 4.5 Krafft temperatures for sodium alkyl sulphates in water

Number of carbon atoms	10	12	14	16	18
Krafft temperature/°C	8	16	30	45	56

Sharpness of CMC

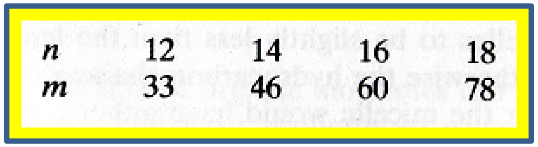
- $mS \;\leftrightarrow\; S_m$: β = fraction of monomer in micelles
  $c(1-\beta) \quad c\beta/m$
- $K = (c\beta/m) / [c(1-\beta)]^m \rightarrow \beta = \beta(c)$ at constant K
- $Kmc^{m-1} = \beta/(1-\beta)^m$
- Typically, m ~ 100 and CMC ~ 10^{-3}.
- β(c) is plotted in the bottom Figure.
  Transition is fairly sharp → lim (m→∞) β(c) is a step function.



Spherical micelle

- Nearly monodispersed.
- The size is limited and it depends on the nature of the lyophobic part of the surfactant.
  $m\,S \leftrightarrow S_m$: S = monomer, S_m = micelle,
  m = aggregation number

n = # of CH_2 unit in a straight chain hydrocarbon



n	12	14	16	18
m	33	46	60	78

- Counter ion binding: counter ion /S < 1

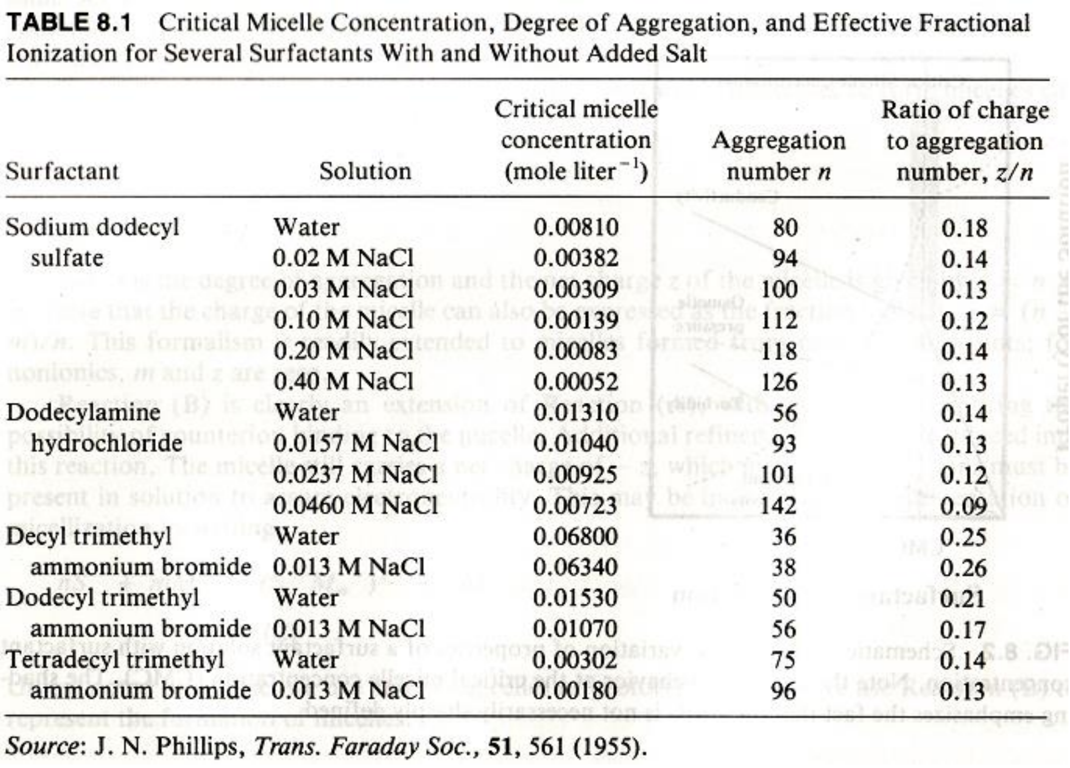
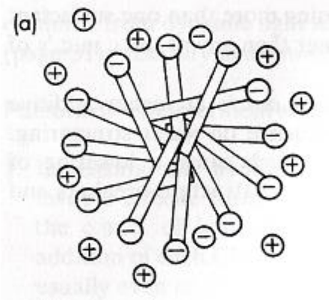


TABLE 8.1 Critical Micelle Concentration, Degree of Aggregation, and Effective Fractional Ionization for Several Surfactants With and Without Added Salt

Surfactant	Solution	Critical micelle concentration (mole liter^{-1})	Aggregation number *n*	Ratio of charge to aggregation number, *z/n*
Sodium dodecyl sulfate	Water	0.00810	80	0.18
	0.02 M NaCl	0.00382	94	0.14
	0.03 M NaCl	0.00309	100	0.13
	0.10 M NaCl	0.00139	112	0.12
	0.20 M NaCl	0.00083	118	0.14
	0.40 M NaCl	0.00052	126	0.13
Dodecylamine hydrochloride	Water	0.01310	56	0.14
	0.0157 M NaCl	0.01040	93	0.13
	0.0237 M NaCl	0.00925	101	0.12
	0.0460 M NaCl	0.00723	142	0.09
Decyl trimethyl ammonium bromide	Water	0.06800	36	0.25
	0.013 M NaCl	0.06340	38	0.26
Dodecyl trimethyl ammonium bromide	Water	0.01530	50	0.21
	0.013 M NaCl	0.01070	56	0.17
Tetradecyl trimethyl ammonium bromide	Water	0.00302	75	0.14
	0.013 M NaCl	0.00180	96	0.13

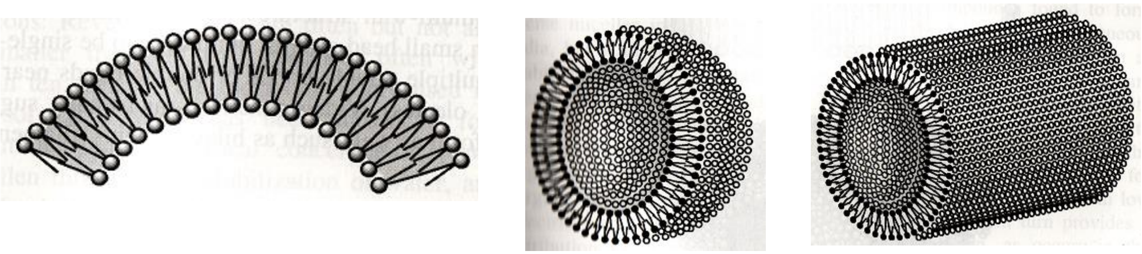
Source: J. N. Phillips, *Trans. Faraday Soc.*, **51**, 561 (1955).

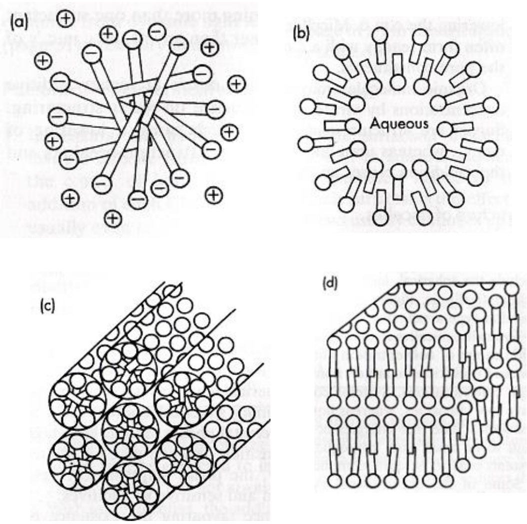


$CH_3(CH_2)_{11}\text{-O-S(-O)}_2\text{-O}^-\text{Na}^+$
Sodium dodecyl sulphate

Structure of micelle

- Spherical, spherical bilayer, hexagonal, lamella
- Typically, micelles tends to be approximately spherical over a fairly wide range of concentration above CMC.
- There are often marked transition to larger, non-spherical liquid crystal structure at high concentrations.





Micelle structures; a) spherical,
b) spherical vesicle bilayer,
c) hexagonal, d) lamella

Evidence for micelle formation

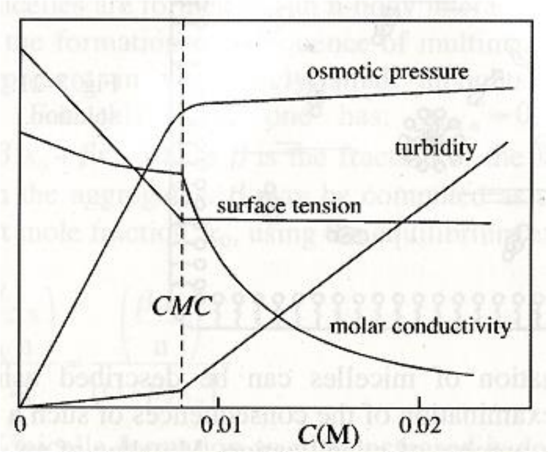
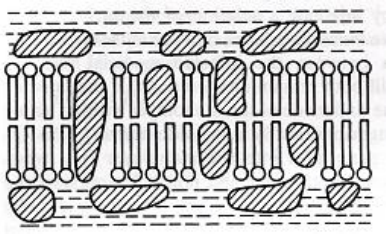


Fig. 3-20: Schematic diagram of physical property changes of aqueous solutions of sodium dodecyl sulfate at 25°C as a function of concentration.

See the next page



Biological cell membrane

Physical property changes at c.m.c.

1. Molar conductivity Λ of ionic surfactants

- Ions contributes to the conductivity but Λ gradually ↓ with increasing concentration because of ion-ion interactions.
- A sharp decrease in Λ above the c.m.c. due to micelle formation.
  1) The total viscous drag is reduced when micelles are formed.
  2) Counter-ions becomes kinetically a part of micelle → the net charge of a micelle z is much smaller than n, reducing the # of counter-ions avail for carrying current.
  3) The electrophoretic retardation effect of the ionic atmospheres of unattached counter-ions is greatly increases.
- the last two effects are responsible for the sharp decrease in Λ when micells are formed.

2. Osmotic pressure Π

- $\pi V = cRT$ (van't Hoff eq.)
- The # of molecules only slightly increases above c.m.c.

3. Turbidity τ

- Turbidity is due the scattering of visible light by particles.
- The scattering power increases with increasing particle size, reaching about maximum when the size is comparable to the wavelength.
- The size of an unassociated surfactant molecule is too small to appreciably scatter visible light.
- When micelle is formed, it can significantly scatter light.

4. Surface tension γ

- Surface tension sharply decreases with increasing surfactant concentration.
- However, when micelle is formed, it's concentration (number-based) increases very slowly.

Factors affecting CMC

1. Hydrophobic chain length n of straight aliphatic surfactant.

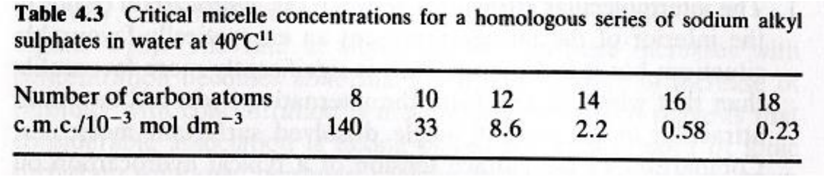


Table 4.3 Critical micelle concentrations for a homologous series of sodium alkyl sulphates in water at 40°C[11]

Number of carbon atoms	8	10	12	14	16	18
c.m.c./10^{-3} mol dm^{-3}	140	33	8.6	2.2	0.58	0.23

ionic: n→ n+1, CMC(n+1)/CMC(n) ~ 1/2

non-ionic: n→ n+1, CMC(n+1)/CMC(n)~ 1/3

log(CMC) = A – Bn : Klevens constants A and B

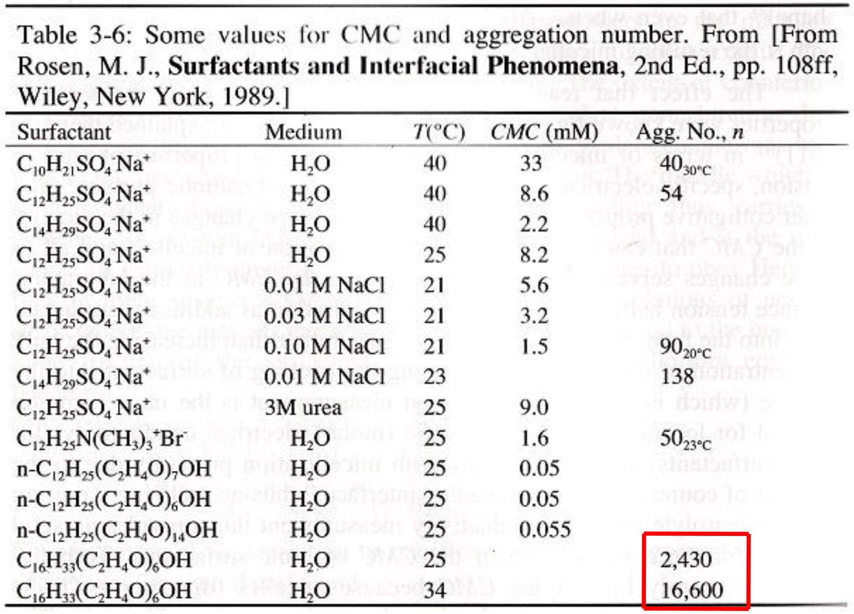
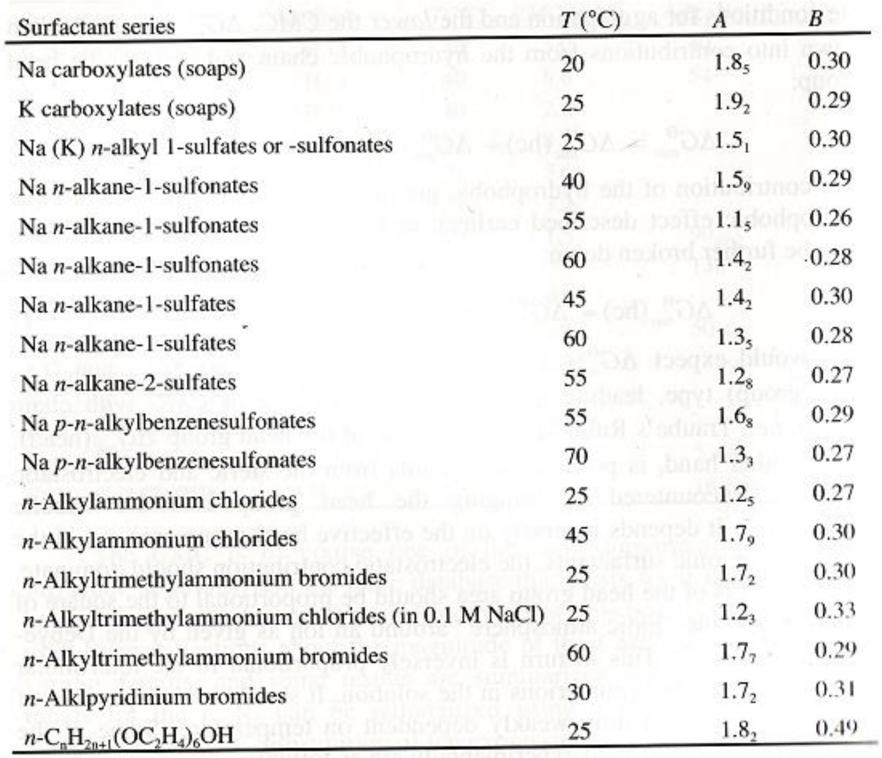


Table 3-6: Some values for CMC and aggregation number. From [From Rosen, M. J., **Surfactants and Interfacial Phenomena**, 2nd Ed., pp. 108ff, Wiley, New York, 1989.]

Surfactant	Medium	*T*(°C)	*CMC* (mM)	Agg. No., *n*
$C_{10}H_{21}SO_4^-Na^+$	H_2O	40	33	$40_{30°C}$
$C_{12}H_{25}SO_4^-Na^+$	H_2O	40	8.6	54
$C_{14}H_{29}SO_4^-Na^+$	H_2O	40	2.2	
$C_{12}H_{25}SO_4^-Na^+$	H_2O	25	8.2	
$C_{12}H_{25}SO_4^-Na^+$	0.01 M NaCl	21	5.6	
$C_{12}H_{25}SO_4^-Na^+$	0.03 M NaCl	21	3.2	
$C_{12}H_{25}SO_4^-Na^+$	0.10 M NaCl	21	1.5	$90_{20°C}$
$C_{14}H_{29}SO_4^-Na^+$	0.01 M NaCl	23		138
$C_{12}H_{25}SO_4^-Na^+$	3M urea	25	9.0	
$C_{12}H_{25}N(CH_3)_3^+Br^-$	H_2O	25	1.6	$50_{23°C}$
n-$C_{12}H_{25}(C_2H_4O)_7OH$	H_2O	25	0.05	
n-$C_{12}H_{25}(C_2H_4O)_6OH$	H_2O	25	0.05	
n-$C_{12}H_{25}(C_2H_4O)_{14}OH$	H_2O	25	0.055	
$C_{16}H_{33}(C_2H_4O)_6OH$	H_2O	25		2,430
$C_{16}H_{33}(C_2H_4O)_6OH$	H_2O	34		16,600

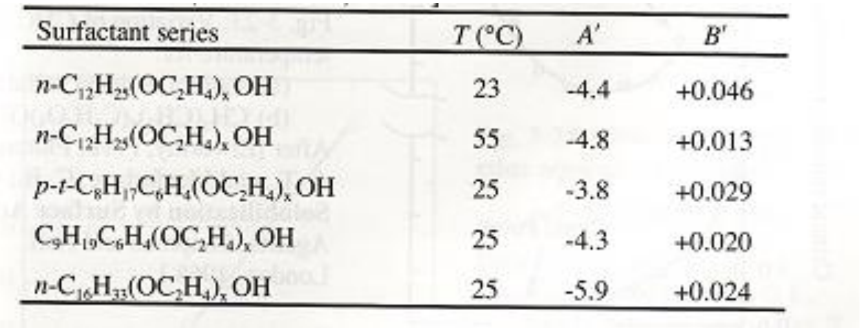
Note: n of nonionic surfactant is much larger

Ionic surfactants



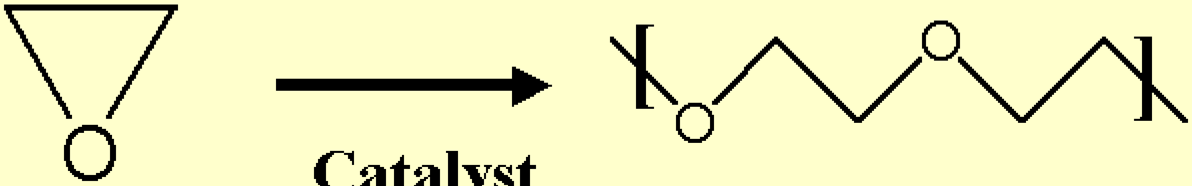
Surfactant series	*T* (°C)	*A*	*B*
Na carboxylates (soaps)	20	1.8_5	0.30
K carboxylates (soaps)	25	1.9_2	0.29
Na (K) *n*-alkyl 1-sulfates or -sulfonates	25	1.5_1	0.30
Na *n*-alkane-1-sulfonates	40	1.5_9	0.29
Na *n*-alkane-1-sulfonates	55	1.1_5	0.26
Na *n*-alkane-1-sulfonates	60	1.4_2	0.28
Na *n*-alkane-1-sulfates	45	1.4_2	0.30
Na *n*-alkane-1-sulfates	60	1.3_5	0.28
Na *n*-alkane-2-sulfates	55	1.2_8	0.27
Na *p*-*n*-alkylbenzenesulfonates	55	1.6_8	0.29
Na *p*-*n*-alkylbenzenesulfonates	70	1.3_3	0.27
n-Alkylammonium chlorides	25	1.2_5	0.27
n-Alkylammonium chlorides	45	1.7_9	0.30
n-Alkyltrimethylammonium bromides	25	1.7_2	0.30
n-Alkyltrimethylammonium chlorides (in 0.1 M NaCl)	25	1.2_3	0.33
n-Alkyltrimethylammonium bromides	60	1.7_7	0.29
n-Alklpyridinium bromides	30	1.7_2	0.31
n-$C_nH_{2n+1}(OC_2H_4)_6OH$	25	1.8_2	0.49

PEO surfactants



Surfactant series	*T* (°C)	*A′*	*B′*
n-$C_{12}H_{25}(OC_2H_4)_x$ OH	23	-4.4	+0.046
n-$C_{12}H_{25}(OC_2H_4)_x$ OH	55	-4.8	+0.013
p-*t*-$C_8H_{17}C_6H_4(OC_2H_4)_x$ OH	25	-3.8	+0.029
$C_9H_{19}C_6H_4(OC_2H_4)_x$ OH	25	-4.3	+0.020
n-$C_{16}H_{33}(OC_2H_4)_x$ OH	25	-5.9	+0.024

Synthesis of polyethylene oxide



Catalyst

Ethylene oxide

PEO

M. Hubbe

2. Type of surfactant

- Nonionic surfactants (PEO type) have lower CMC's than ionic ones for the same HC chain length and temperature: ~ an order of magnitude.
- Micelle formation of ionic surfactants is less favored because of the electrostatic repulsion between adjacent charged head groups.

3. Presence of electrolytes

- For ionic surfactants, addition of electrolytes(salts) lowers CMC.
- Counter ions (of added salt) near the head groups reduce the electrostatic repulsion, and therefore micelle formation is more favored.

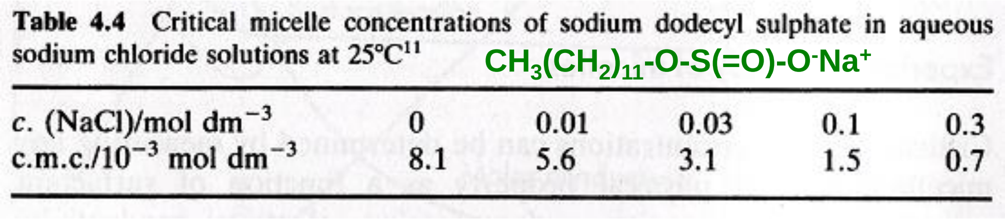


Table 4.4 Critical micelle concentrations of sodium dodecyl sulphate in aqueous sodium chloride solutions at 25°C[11]

$CH_3(CH_2)_{11}$-O-S(=O)-O^-Na^+

c. (NaCl)/mol dm^{-3}	0	0.01	0.03	0.1	0.3
c.m.c./10^{-3} mol dm^{-3}	8.1	5.6	3.1	1.5	0.7

4. Temperature

- Micelle formation is opposed by thermal agitation and CMC is expected to increases T↑. This is not always the case.
- T-dependence is, in general complex because of various competing factors
- For ionic surfactant, the dependence is weak over a significant T-range.
- For nonionic surfactant (PEO type), CMC sharply↓ with T↑ due to the progressive dehydration of the PEO groups (Fig.3-23 b) until a point (Cloud point) is reached where very large micelles are formed, producing visible turbidity.
- The transition occurring at cloud point is sharp like a macroscopic phase transition.

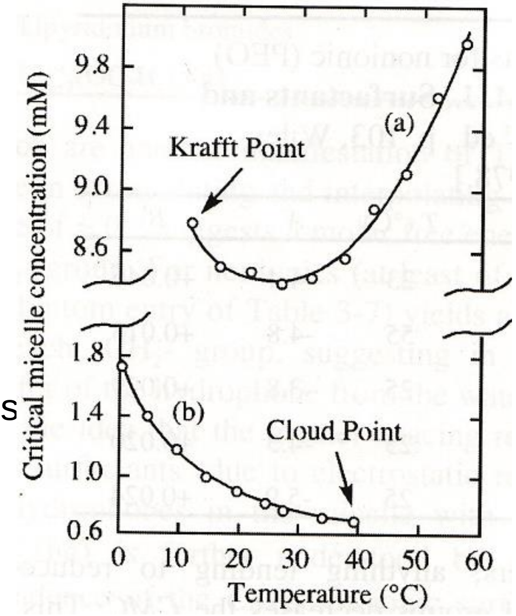


Fig. 3-23: Variation of *CMC* with temperature for:
(a) sodium dodecyl sulfate;
(b) $CH_3(CH_2)_9(C_2H_4O)_5OH$

Energetics of micellization

Interactions involved in micelle formation

Monomer

- Hydrophobic effect (breaking H-bonds among H_2O molecules (1)
- Hydration of the hydrophilic groups (2)
- Entropy of monomers wrt. Micelle (2)

Micelle

- Electrostatic repulsion between adjacent ionic head groups (1)
- Significant entropy of hydrophobic chains (1),

where (1) favors micellzation, while (2) disfavors it.

$\mathbf{mS} \leftrightarrow \mathbf{S_m}$ **;** $K = (c\beta/m) / [c(1-\beta)]^m$ **;** $\beta =$ the fraction of total monomers in micelles

$\Delta G^0 = - RT \ln K$

Per mole of monomer, $\Delta G^0 = - RT \ln K /m$

$$= - (RT/m) \ln(c\beta/m) + RT \ln [c(1-\beta)] = RT [- \{ \ln(c\beta/m) \}/m + \ln \{c(1-\beta)\}]$$

At CMC, $\beta \sim 0$ and the <u>1st term ~ 0</u> because of a large m. Therefore,

$\Delta G^0 = RT \ln(CMC)$

$dG = VdP - SdT$, and $\Delta S^0 = - (\partial G^0/\partial T)_p$

$\Delta S^0 = - d(\Delta G^0)/dT = - RT\, d \ln(CMC)/dT - R \ln(CMC)$

$\Delta H^0 = \Delta G^0 + T \Delta S^0$

$= - RT^2\, d \ln(CMC)/dT$

- In general, CMC ↑ with T↑, meaning that micellization process is an exothermic process.
- As stated earlier, it is not always the case (ref. Fig.3-2 a).
- This suggests that the entropy of a micelle is not small, i.e., the inner hydrophobic part has significant freedom (motion).

TABLE 8.3 Some Thermodynamic Properties for the Micellization Process at or Near 25 °C for Various Surfactants

Surfactant	ΔG^0_{mic} (kJ mole^{-1})	ΔH^0_{mic} (kJ mole^{-1})	ΔS^0_{mic} (J K^{-1} mole^{-1})
Dodecyl pyridinium bromide	−21.0	−4.06	+56.9
Sodium dodecyl sulfate[a]	−21.9	+2.51	+81.9
N-Dodecyl-*N*,*N*-dimethyl glycine	−25.6	−5.86	+64.9
Polyoxyethylene(6) decanol	−27.3	+15.1	+142.0
N,*N*-Dimethyl dodecyl amine oxide	−25.4	+7.11	+109.0

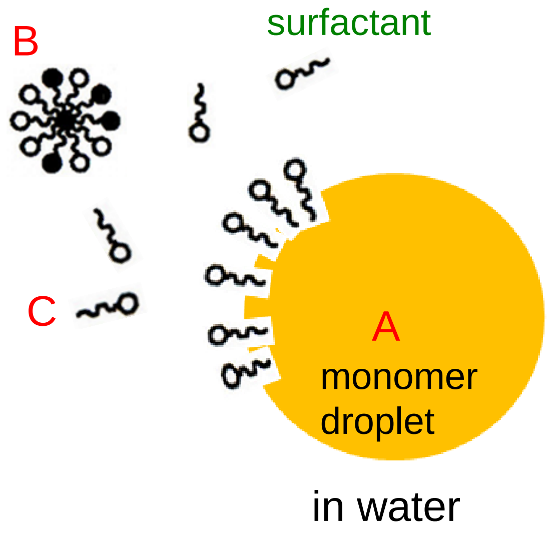
Source: Data from J. H. Fendler and E. J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, 1975.

[a] Calculated in Example 8.4.

Solubilization

- Surfactant solutions above the CMC can solubilize otherwise insoluble organic material by incorporating it into the interior of micelles.
- Examples: the dye xylenol orange disolves only sparingly in pure water but gives a deep red solution with sodium dodecyl sulphate present above its CMC.
- Of practical importance in many applications;
  1) formulation of pharmaceutical and other water-insoluble ingredients,
  2) detergency (removal of oily soil),
  3) emulsion polymerization
  4) micellar catalysis

Emulsion polymerization: Harkins model



- Ex: polymerization of polystyrene
- Monomer distribution
  A: monomer droplet
  B: inside a micelle (solubilized)
  C: in water (dissolved, isolated)
- Polymerization occurs within micelles
  size and shape (spherical bead) regulation
- Radical polymerization
- Initiators(R·) formed in water, combining with dissolved monomers to form RM· → transferred into micelles; the probability of diffusion into a micelle is much greater than that into a monomer droplet because of much larger surface areas of micelles.

Spreading

Adhesion and cohesion

Dupré equation

- Work of adshesion $W_a = \gamma_A + \gamma_B - \gamma_{AB}$
- Work of cohesion $W_c = \gamma_A + \gamma_A - \gamma_{AA} (= 0) = 2\gamma_A$

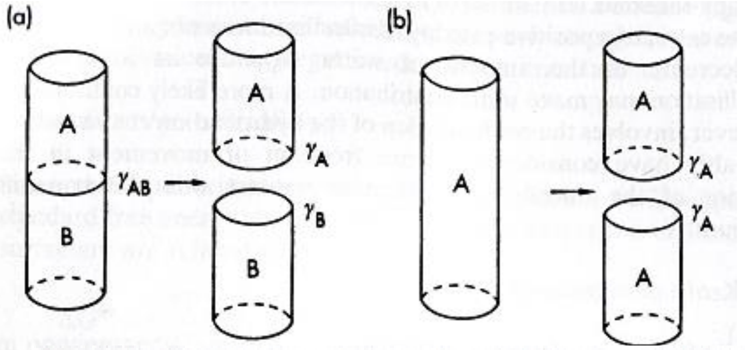
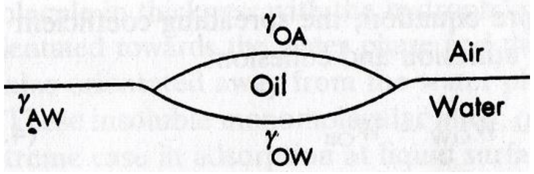


Figure 4.15 Work of adhesion (a) and of cohesion (b)

Spreading of one liquid on another

- When a drop of an insoluble oil is placed on a clean water surface it may
  1) remain as a lens (non-spreading)
  2) spread as a thin film until it is uniformly distributed over the surface as a duplex film (a film thick enough for the two interface to be independent and posses characteristic surface tension)
  3) spread as a monolayer, leaving excess oil as lenses in equilibrium (Fig.4.17)
- If the lens in Fig, 4.16 is very thin, a contact area change of dA is accompanied by
  $dG = [(\gamma_O + \gamma_{OW}) - \gamma_W]\, dA = - S\, dA$

Figure 4.16 A drop of non-spreading oil on a water surface



Initial spreading coefficient S

$S = \gamma_W - (\gamma_O + \gamma_{OW})$: oil on water

- If dG < 0 or S > 0: spontaneous spreading
- If dG > 0 or S < 0 :contraction of the lens
- If dG = 0 or S = 0 : equilibrium

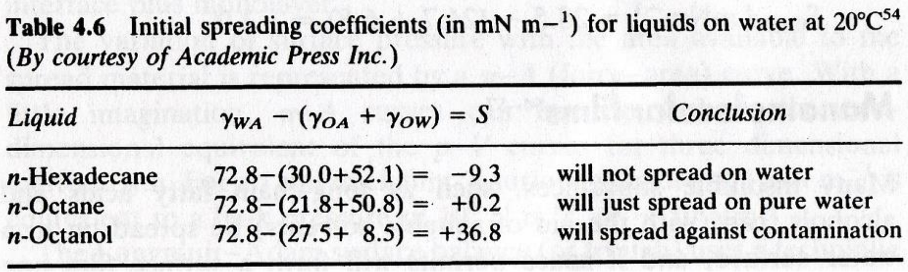


Table 4.6 Initial spreading coefficients (in mN m^{-1}) for liquids on water at 20°C[54] *(By courtesy of Academic Press Inc.)*

Liquid	$\gamma_{WA} - (\gamma_{OA} + \gamma_{OW}) = S$	*Conclusion*
n-Hexadecane	72.8−(30.0+52.1) = −9.3	will not spread on water
n-Octane	72.8−(21.8+50.8) = +0.2	will just spread on pure water
n-Octanol	72.8−(27.5+ 8.5) = +36.8	will spread against contamination

Spreading (cont'd)

- Substituting in the Dupré equation,

$$S = \gamma_W - (\gamma_O + \gamma_{OW}) = \gamma_W + \gamma_O - \gamma_{OW} - 2\gamma_O = W_{ow} - W_{oil}$$

Factors influencing spreading

Impurities

- Impurities in water lowers γ_W more than it does γ_{OW}, especially if γ_{OW} is already low.

  ex: $S_{initial} = 0.2$ for n-octane on pure water

  $S_{initial} < 0$ for n-octane on contaminated water

Mutual saturation of one liquid with another

- The solubility of oil in water or vice versa at room temperature is small. However, the reduction in γ_W may be significant enough to affect spreading.
- Ex: Benzene on water

  $S_{initial} = 72.8 - (28.9 + 35.0) = 8.9 > 0$; spreading

  $S_{final} = 62.4 - (28.8 + 35.0) = -1.4 < 0$; non-spreading
- Initial spreading stops, and the film may retract slightly to form very flat lens.

- Ex: n-hexanol on water

  $S_{initial} = 72.8 - (28.9 + 35.0) = 8.9 > 0$; spreading

  $S_{final} = 28.5 - (24.7 + 6.8) = -3.0 < 0$; non-spreading

The final state is shown in Fig. 4.17

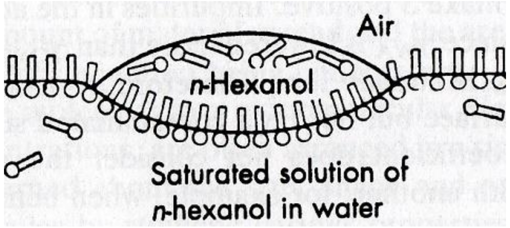


Figure 4.17 Spreading of *n*-hexanol on a water surface

Monomolecular Film

Insoluble (Langmuir) monolayer

- Surfactant molecules adsorb at the surface, resulting in the reduction of the surface tension.
  $\gamma_0 - \gamma = \pi$, where π is the spreading pressure

- The spreading pressure can be measured using a surface balance (Fig. 4.18).
- The surfactant molecules form a monolayer film.

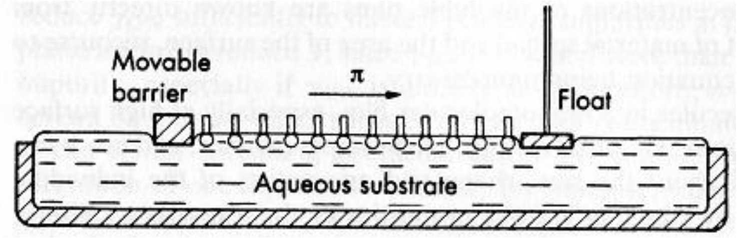


Figure 4.18 The principle of the Langmuir–Adam surface balance

Physical states of monomolecular films

- The monolayers can be roughly classified as

1. Condensed (solid) films

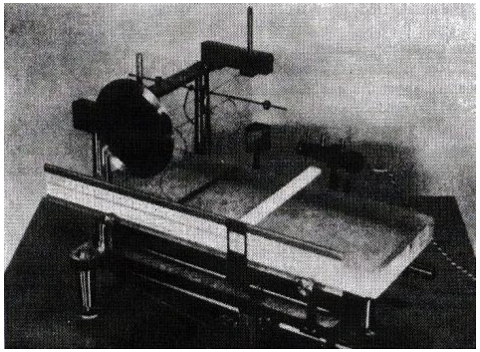
- Closely packed film with molecules steeply oriented towards the surface.

2. Liquid states

- Films are still coherent but occupy a much larger area than condensed films.
- It is like a highly compressible liquid, in this sense there is no real 3D equivalent.
- There exist a number of different expanded films, the most important being the liquid-expanded state.

3. 2D Gaseous films

- Molecules are separate and move about the surface independently.
- Surface pressure is exerted on the 2D barrier by a series of collisions



Gaseous films

- Molecules in a gaseous film behaves like a 2D gas.
- Equation of state:

$\Gamma_2 = - c_2 / RT\, (d\gamma / dc_2)$, where Γ_2 is in mole/unit surface area.

$\pi = \gamma_0 - \gamma = bc_2$ at low concentration, and $d\gamma / dc_2 = - b = - \pi / c_2$.

$\Gamma_2 = - c_2 / RT\, (- \pi / c_2) = \pi / RT$,

$\Gamma_2 = n_2\,(\text{mole}) / \mathcal{A} = N_2\,(\text{molecules}) / \mathcal{A} N_A = \pi / RT = \pi / RT$

$\mathcal{A} N_A / N_2 = RT / \pi \rightarrow \mathcal{A} / N_2 = kT / \pi$

Let **A** be the average surface area taken by a molecule, $A = \mathcal{A} / N_2$

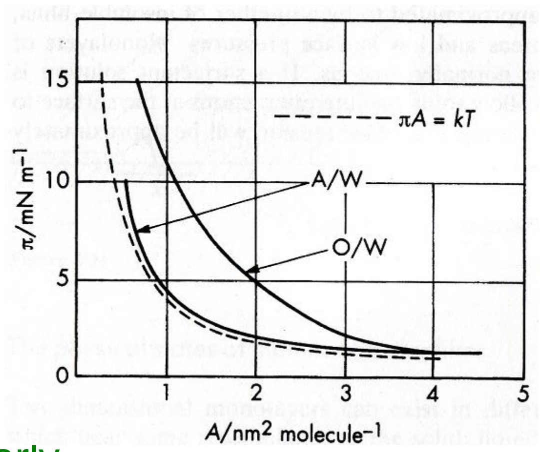
$\boxed{\pi A = kT}$

- It is just a 2D ideal gas law.
- As for 3D van der Waals equation,
- $(\pi - \pi_0)(A - A_0) = kT$ is more appropriate for real gases.

- Ex: For CTAB (cetyl trimethyl ammonium bromide) $C_{16}H_{33}N(CH_3)_3^+Br^-$ at water- air interface, $\pi A = kT$ approximately holds, for

- The electrostatic repulsion between the ionic head group is nearly compensated by the attractive force between the alkyl chains.

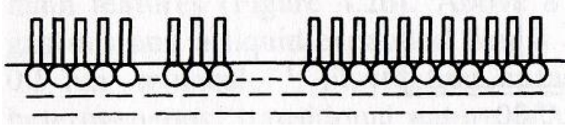
- At water-oil interface, π is much larger for a given A because the repulsion $F = q^2 / 4\pi\varepsilon r$ is much stronger due to a smaller dielectric constant $\varepsilon_r (= \varepsilon / \varepsilon_0)$ of the oil.



π – A curves for CTAB at Water-air and water-oil Interfaces at 20 °C

Condensed films

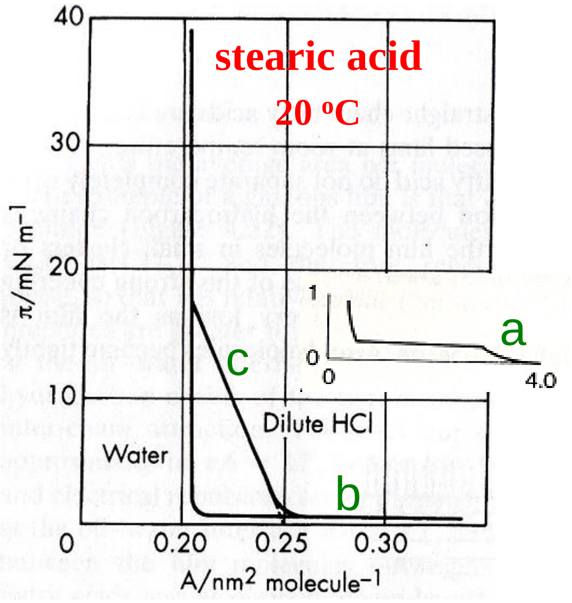
Fig. 4.23



- Higher straight chain fatty acids such as stearic acid $CH_3(CH_2)_{16}COOH$ and palmitic acid$CH_3(CH_2)_{14}COOH$ are examples of condensed films.
- The cohesion (attractive interaction) is strong for these molecules, thus forming clusters and islands (Fig. 4.23) .
- Because of this strong cohering tendency the surface pressure remains very low as the film is compressed and then rises rapidly when the molecules become tightly packed together.

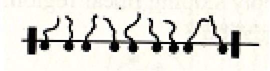
Ex: **π – A** curves for stearic acid spread on HCl solution at 20 °C (bottom Fig)

- At very low pressure molecular orientation is random and tilted (a)
- In the horizontal region the molecules are lifted up (b). The compressibility is large (easily compressible) and the pressure rise is very small.
- Initial pressure rise at **$0.25\ nm^2$** → initial packing of end groups.
- **π – A** curve becomes very steep at **$0.205\ nm^2$** → more efficient packing by staggering and interlocking of the end groups.



- Limiting surface are = $0.20\text{-}0.22\ nm^2$ for straight chain fatty acid irrespective of the chain length.
- This value is close to the cross-section of crystalline SA measured by X-ray diffraction.
- Further compression beyond this limit will eventually lead to collapse or buckling of the film.

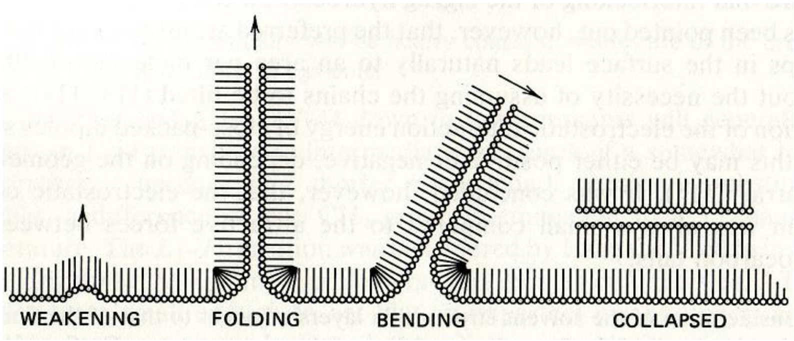
a) expanded

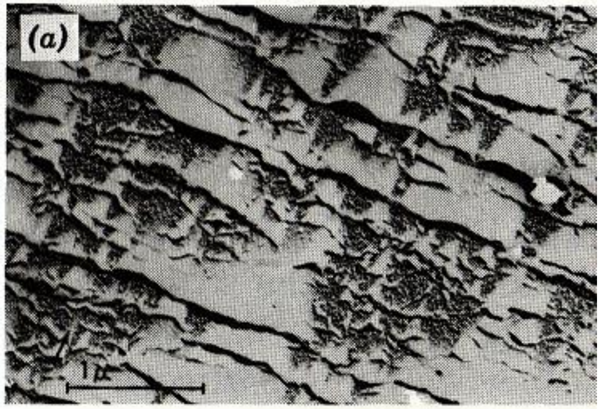


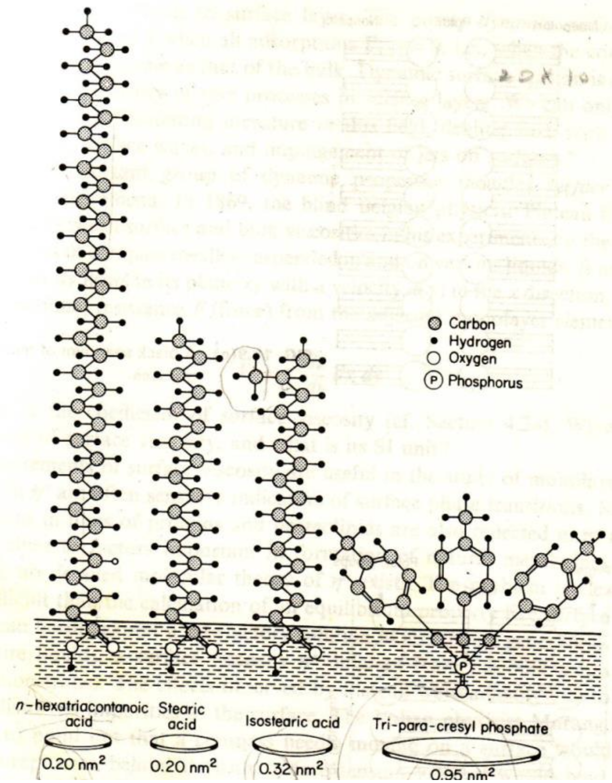
b) partially compressed

c) compressed

Various forms of film deformation beyond the elastic limit.





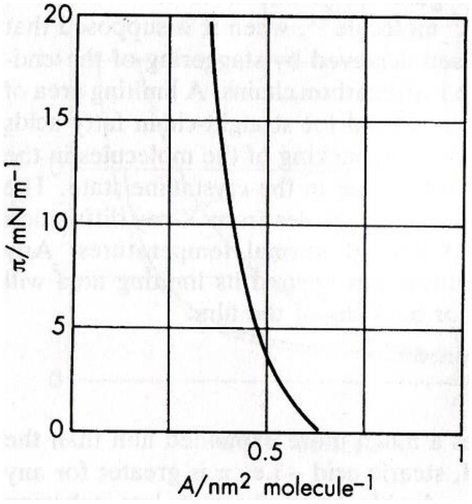


Cross-sectional areas of various surfactant molecules measures from the $\pi - A$ curves

Expanded films

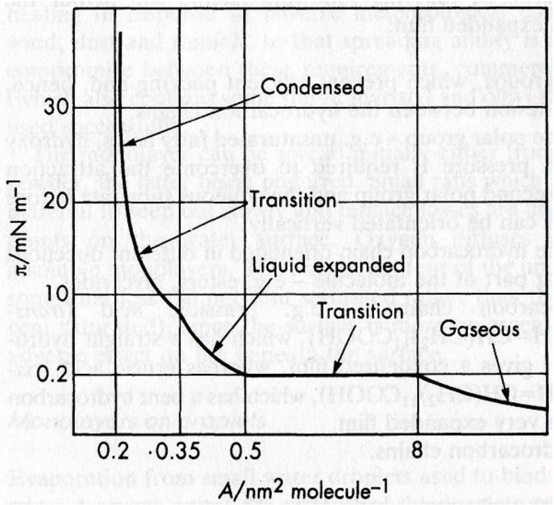
Oleicacid
$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$

- Oleicacid gives a much more expanded film than the corresponding saturated acid, stearic acid.
- Because of the double bond there is less cohesion between the hydrocarbon chains than the stearic acid and a greater affinity for the aqueous surface.
- So π is larger for a given A .



π – A curve for oleicacid on water at **20 ºC**

- The **π – A** curve for myristicacid,$CH_3(CH_2)_{12}COOH$, spread on 0.1 M HCl at **14 ºC** (bottom Fig.) shows its overall resemblance to the p-V curve of a 3D real gas.
- But the liquid expanded state has no 3D equivalent.



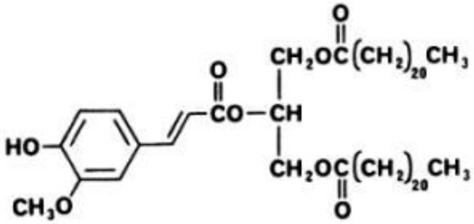
Factors influencing the physical state of monomolecular films

- Lateral cohesion between the end groups(attraction)
- Cohesion depends on the geometry and orientation of the HC chain
- Affinity for the aqueous phase (attraction)
- A longer HC chain has a higher tendency for cohesion
- The transition temperature is lowered by ~ 5- 8 ^oC by adding one more CH_2 group.

The following factors will favor the formation of an expanded films;

1. Bulky head groups (ex: $-SO_4$, $- PO_4$) prevent efficient packing and, hence, maximum cohesion between the HC chains.
2. More than one polar head groups- e.g. unsaturated fatty acids, hydroxy acids.
3. More than one HC chain oriented in different directionsn for the polar part of the molecule- e.g. esters, glycerides
4. Bent HC chains gives very expanded films.
5. Branched HC chains.
6. The nature of the substrates.

- PH is very important for ionizable monolayers.
- The repulsion between ionized COO^- groups favors the formation of gaseous or liquid-expanded films at low T.
- Dissolved electrolytes have a profound effect on the state of the film; Ex: Ca2+ ions form insoluble calcium soaps with fatty acid films (unless the pH is very low), thus making the film more condensed.



triiglyceride

Film deposition

Langmuir-Blodgett film

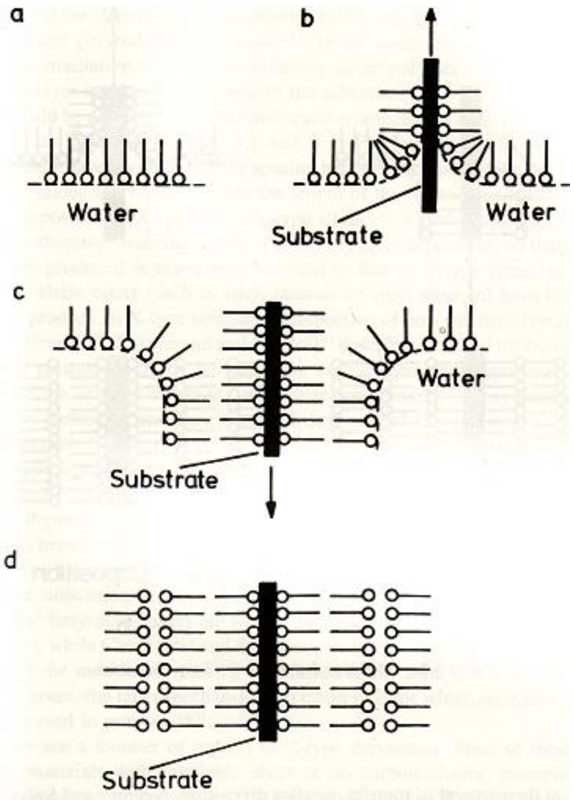


Figure 3.1. Y-type Langmuir–Blodgett film deposition.

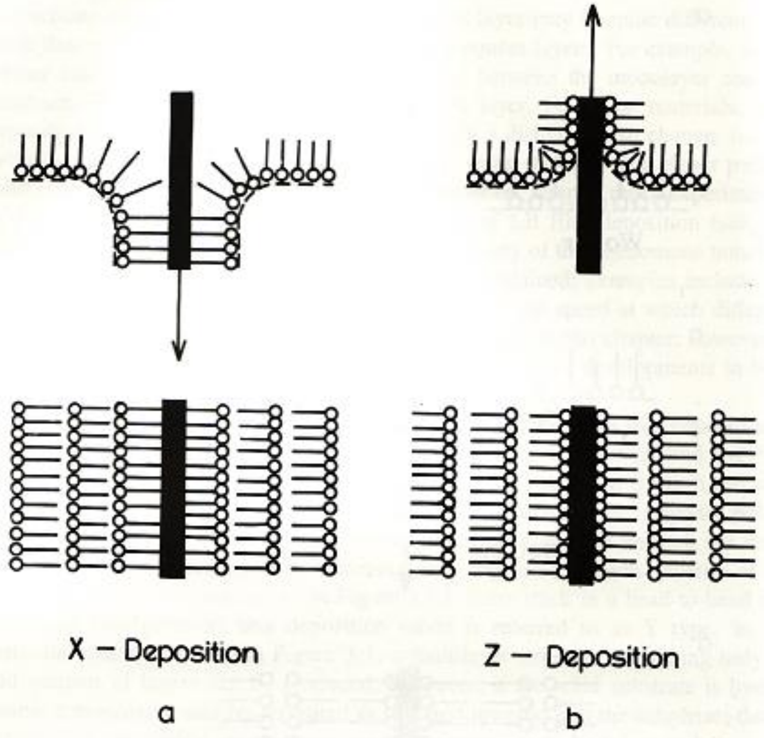


Figure 3.2. (a) X-type deposition; (b) Z-type deposition.

Controlling parameters: pH, surface pressure etc.