Liquid Interfaces

1. Surface energy and surface tension (5.2.1)
2. Liquid surfaces (5.2.2-)
3. Liquid films (5.3, 5.4, 5.5, 5.6)
4. Thermodynamics of liquid Interfaces (5.7)
5. Electrified and charged Interfaces (5.1, 5.8)

Reading: Kolasinski, ch.5,
Somorjai, ch.3, Shaw, ch. 4
Pashley

Surfactants, Langmuir films, Langmuir-Blodgett films,
self assembly monolayers
(5.3, 5.4, 5.5, 5.6)
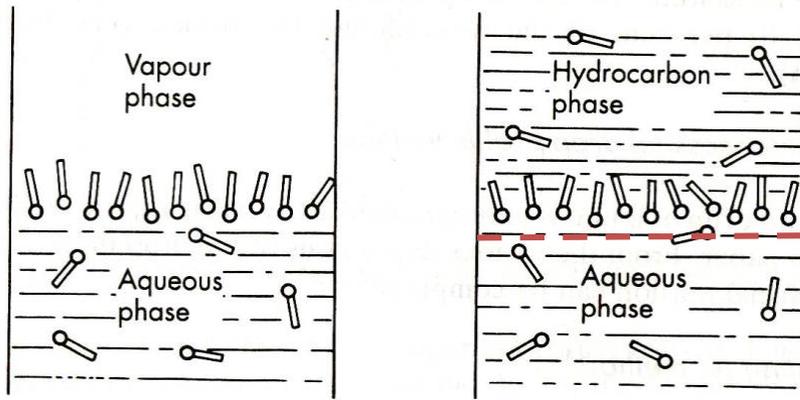
Surface tension of 2-component systems
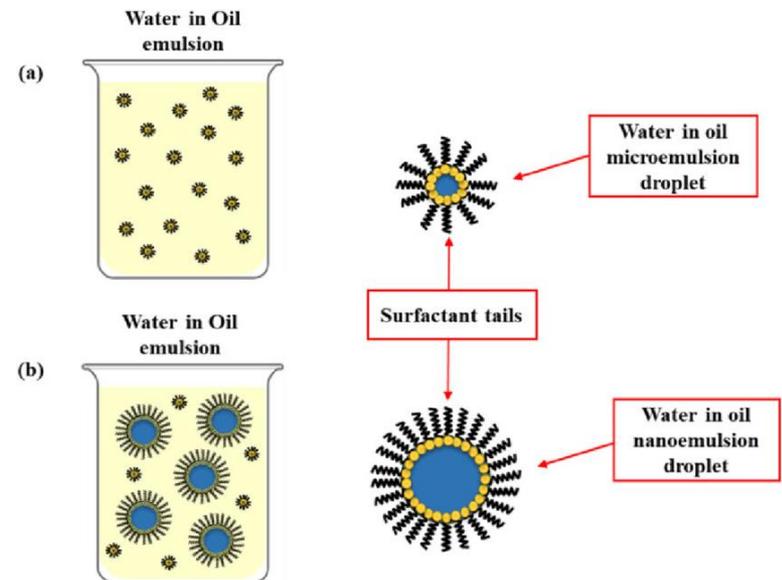
Surface activity

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

π : surface pressure (expanding pressure)

Surface active agent, surfactant : $\gamma\downarrow$

$\gamma\downarrow \rightarrow$ emulsification
If $\pi \geq \gamma_0$ microemulsion

Adsorption and orientation at interfaces

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.
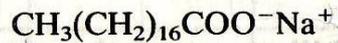- Surfactants are used in many important industrial applications

head

tail
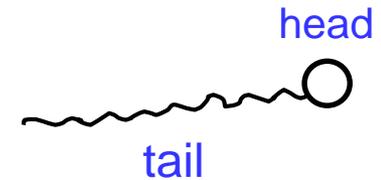
Classification of surfactant
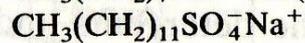
Table 4.2 Surface-active agents

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	$CH_3(CH_2)_{11}.C_6H_4.SO_3^-Na^+$

Most widely used (low cost, performance)

Cationic	
Dodecylamine hydrochloride	$CH_3(CH_2)_{11}NH_3^+Cl^-$
Hexadecyltrimethyl ammonium bromide	$CH_3(CH_2)_{15}N(CH_3)_3^+Br^-$

expensive

Non-ionic	
Polyethylene oxides	e.g. $CH_3(CH_2)_{11}(O.CH_2.CH_2)_6OH^*$
Spans (sorbitan esters)	
Tweens (polyoxyethylene sorbitan esters)	
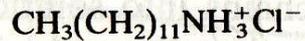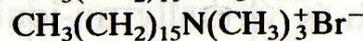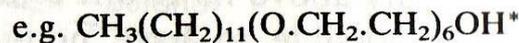
Surfactant:
Synthetic detergent
Wetting agent
Emulsifier
dispersant

Ampholytic (amphiphilic)   dodecyl betaine $C_{12}H_{25}N^+$ $(CH_3)_2$ CH_2COO^-
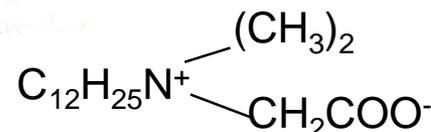
Self-assembly of surfactant: Micelle formation

Micelle: organized aggregates

• 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

T↑ → solubility↑,   longer chain: insoluble

Micellization: alternative mechanism to adsorption by
which the interface energy of surfactant solution might
decrease

Vapour phase

Aqueous phase
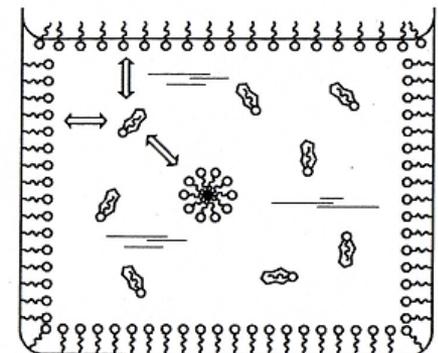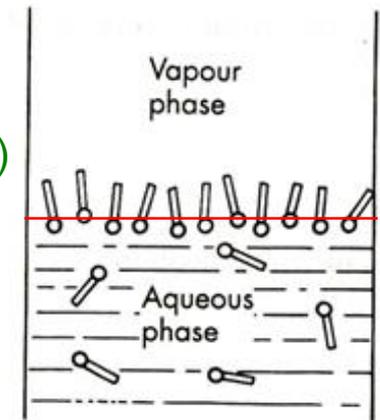
NaCl solution
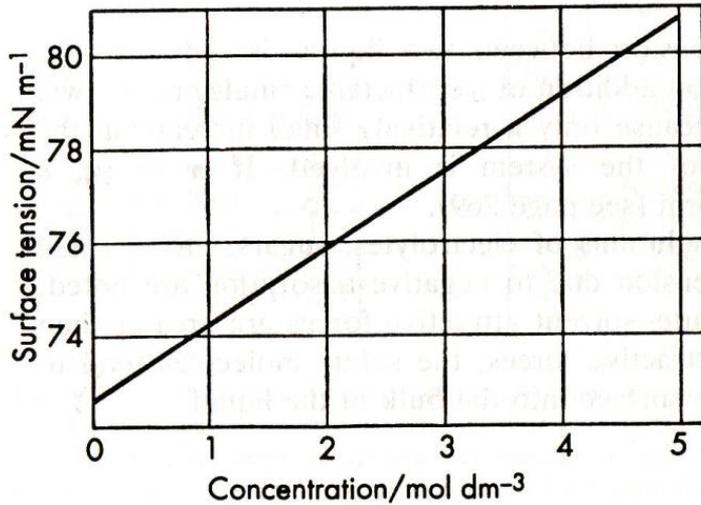
Electrolyte↑ or sugar↑ → γ↑
Negative adsorption:
Solute-solvent > solvent-solvent
attractive force   attractive force

Alcohol in water
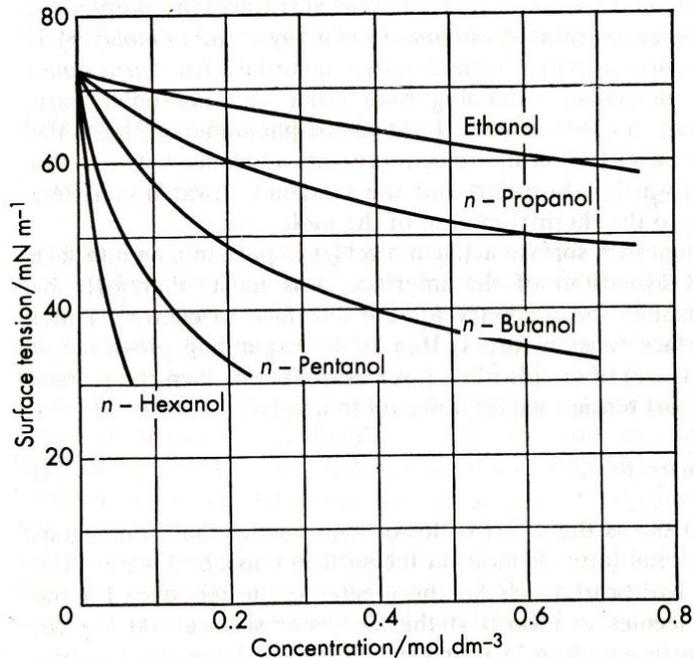
One CH$_3$ group↑ →
1/3 of concentration to get same γ
                    (Traube's rule)
Longer HC chain →
surface activity (adsorption at interface)↑
→ γ↓

Sharpness of CMC

- $mS \leftrightarrow S_m$: β = fraction of monomer in micelles
  $c(1-\beta)$ $c\beta/m$ c: solution concentration, m: # of monomer per micelle

- $K = (c\beta/m) / [c(1-\beta)]^m \rightarrow \beta = \beta(c)$ at constant K
- $Kmc^{m-1} = \beta/(1-\beta)^m$
- Typically, m ~ 100 and CMC ~ 10^{-3}.
- $\beta(c)$ is plotted in the bottom Figure
  Transition is fairly sharp $\rightarrow \lim (m\rightarrow\infty)$ $\beta(c)$ is a step function

lim
m→∞
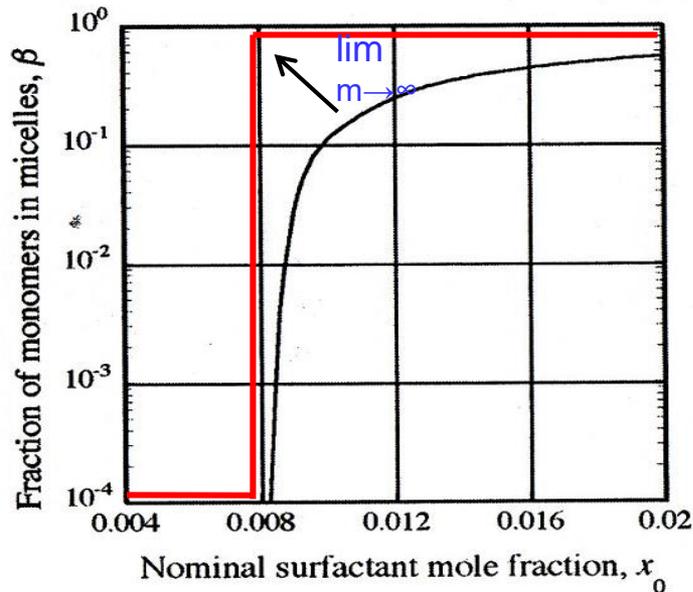
Spherical micelle

• 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

• Counter ion binding: counter ion /S < 1

n = # of CH_2 unit in a straight chain hydrocarbon

n	12	14	16	18
m	33	46	60	78

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).

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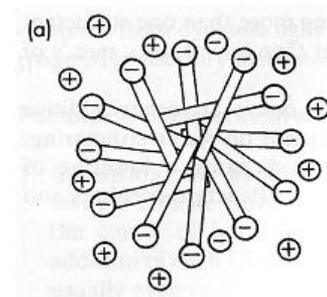
$CH_3(CH_2)_{11}\text{-O-S(-O)}_2\text{-O}^-Na^+$
Sodium dodecyl sulphate

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.
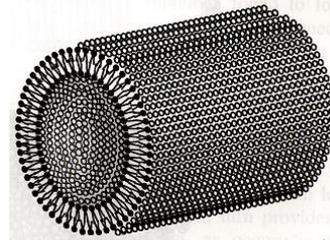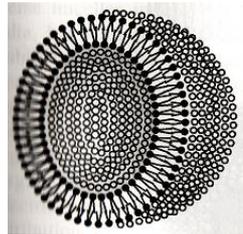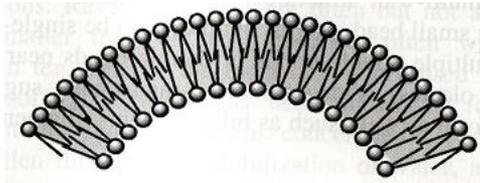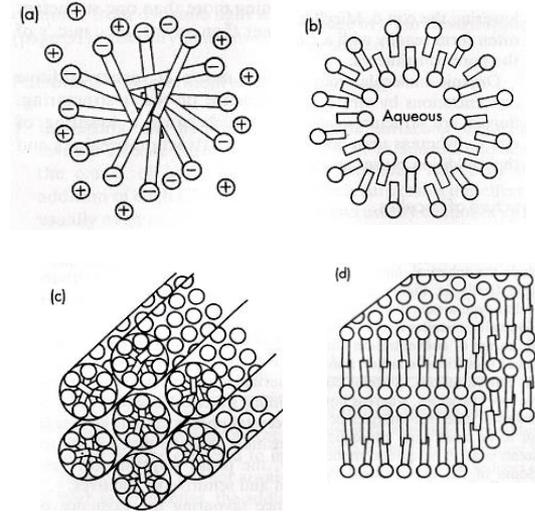
Micelle structures; a) spherical, b) spherical vesicle bilayer, c) hexagonal, d) lamella
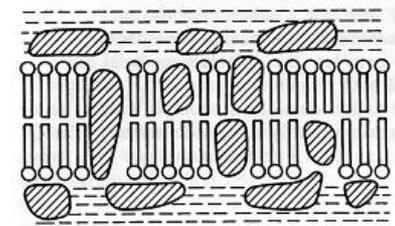
Biological cell membrane

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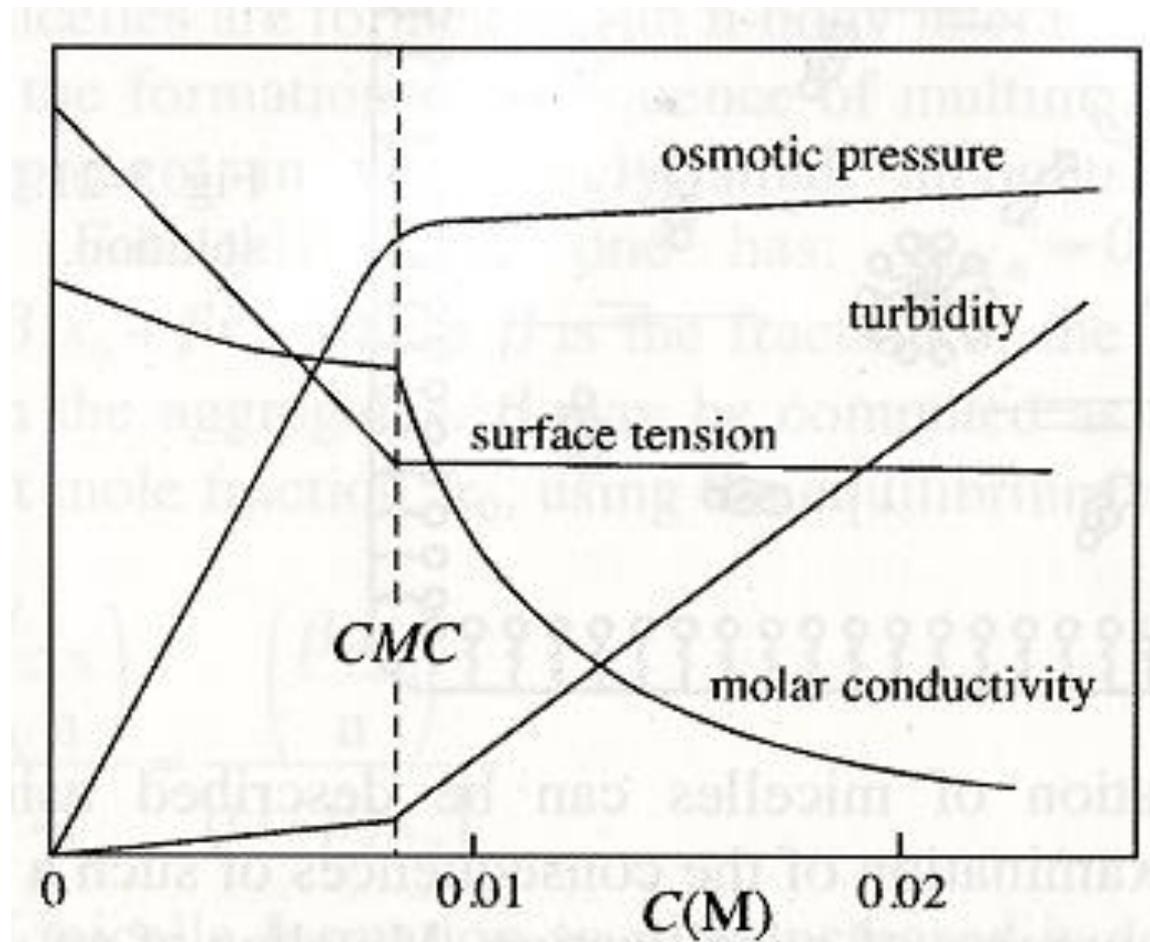
Fig. 3-20: Schematic diagram of physical property changes of aqueous solutions of sodium dodecyl sulfate at 25°C as a function of concentration.

Physical property changes at cmc

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 available 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 micelles 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: $n \rightarrow n+1$, CMC(n+1)/CMC(n) ~ 1/2
non-ionic: $n \rightarrow n+1$, 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

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

Surfactant series	T (°C)	A'	B'
$n-C_{12}H_{25}(OC_2H_4)_xOH$	23	-4.4	+0.046
$n-C_{12}H_{25}(OC_2H_4)_xOH$	55	-4.8	+0.013
$p-t-C_8H_{17}C_6H_4(OC_2H_4)_xOH$	25	-3.8	+0.029
$C_9H_{19}C_6H_4(OC_2H_4)_xOH$	25	-4.3	+0.020
$n-C_{16}H_{33}(OC_2H_4)_xOH$	25	-5.9	+0.024

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.
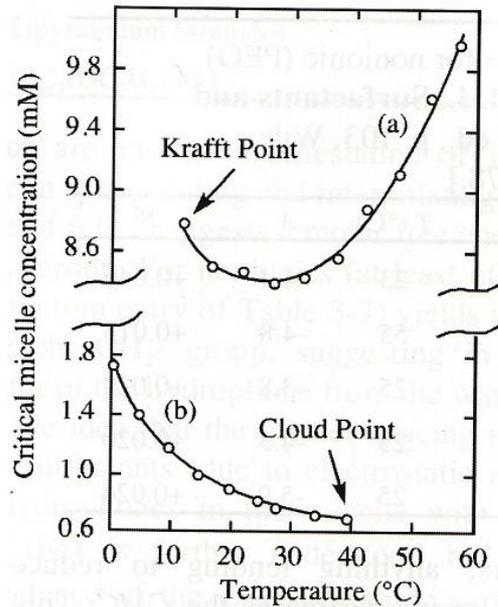- The transition occurring at cloud point is sharp like a macroscopic phase transition.

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

At lower T
Enthalpy of micellization > 0 (endothermic)
→ micellization is entropy directed

5. Addition of organic molecules

e.g. alcohol → reduced electrostatic repulsion & steric hindrance →cmc↓
  sugar → structure makers (water structuring) → cmc↓
  urea or formamide → structure breakers → cmc↑

Energetics of micellization

Interactions involved in micelle formation

Monomer
- Hydrophobic effect (breaking H-bonds among H_2O molecules
- Hydration of the hydrophilic groups
- Entropy of monomers with respect to micelle

Micelle
- Electrostatic repulsion between adjacent ionic head groups
- Significant entropy of hydrophobic chains,

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

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

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

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

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

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

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

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

$\Delta H^0 = \Delta G^0 + T\Delta S^0 = -RT^2\, d\ln(CMC)/dT$

• In general, CMC ↑ with T↑, → micellization process is an exothermic process.
• As stated earlier, it is not always the case.
• 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 of organic reactions

Emulsion polymerization: Harkins model

• e.g.: 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.

surfactant

B

C

A

monomer droplet
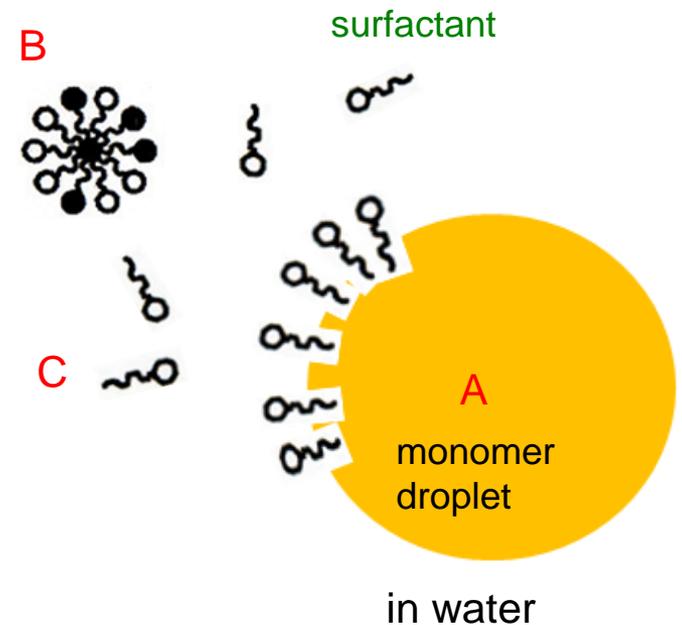
in water

Spreading

Adhesion and cohesion

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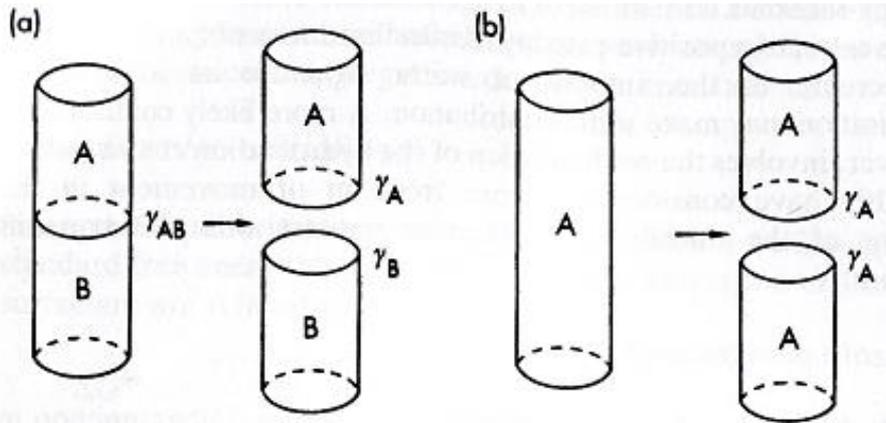

Figure 4.15 Work of adhesion (a) and of cohesion (b)

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

$$dG = [(\gamma_O + \gamma_{OW}) - \gamma_W] \, dA = - S \, dA$$

Initial spreading coefficient S

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

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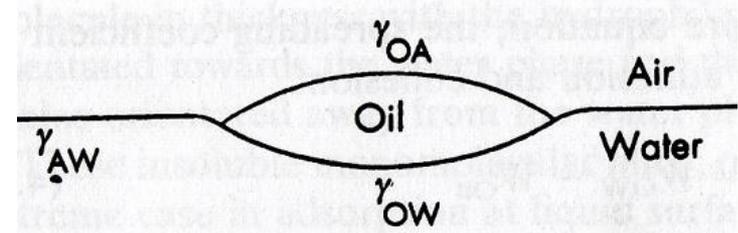• If dG = 0 or S = 0 : equilibrium

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

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

Additivity of intermolecular force

$$\gamma_W = \gamma_W^d + \gamma_W^h$$ Dispersion force (van der Waals) + hydrogen bonding

$$\gamma_{Hg} = \gamma_{Hg}^d + \gamma_{Hg}^m$$ Dispersion force (van der Waals) + metal bonding

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

Ex: n-hexane-water interface   Hydrocarbon: Dispersion force only

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

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

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

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

H$_2$O, Hg → high γ
hydrogen bonding,
Metal bonding

Liquid	γ_O	γ_i	Liquid	γ_O	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

Spreading (cont'd)

Spreading occurs when oil adheres to the water were strongly than it coheres to itself,

$$W_a = W_{OW} = \gamma_O + \gamma_W - \gamma_{OW}$$
$$W_C = W_O = 2\gamma_O$$

- 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

n-octane spread on clean water surface, not on contaminated water
Impurity in oil: $\gamma_{OW}\downarrow \rightarrow S > 0$

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
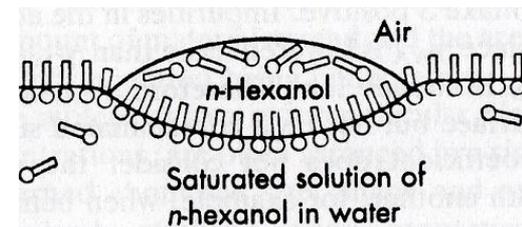
  The final state is shown in Fig. 4.17

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.

$$\gamma_0 - \gamma = \pi \text{ , where } \pi \text{ is the spreading pressure}$$

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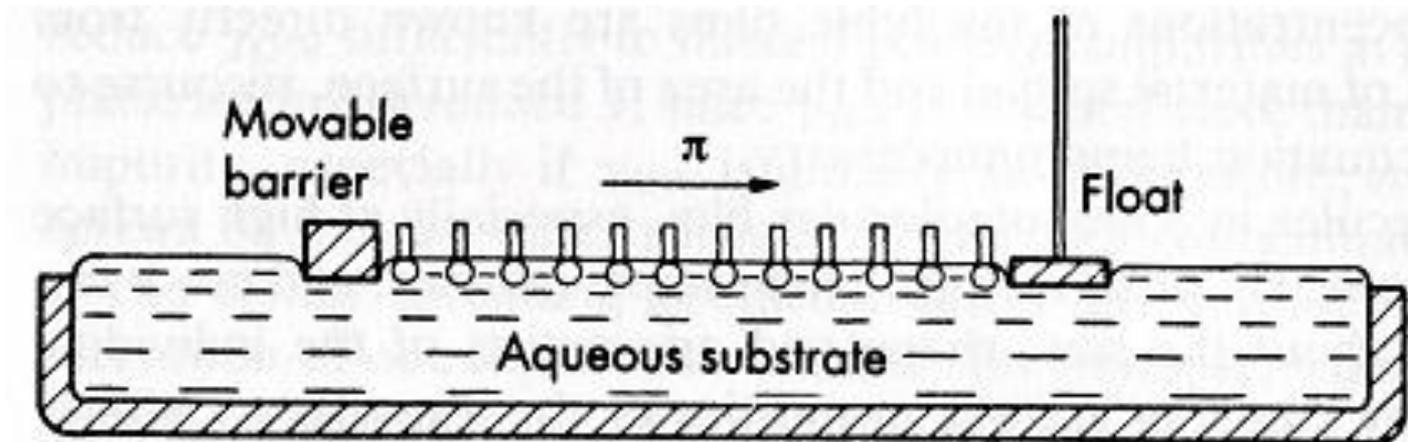• The surfactant molecules form a monolayer film.

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.
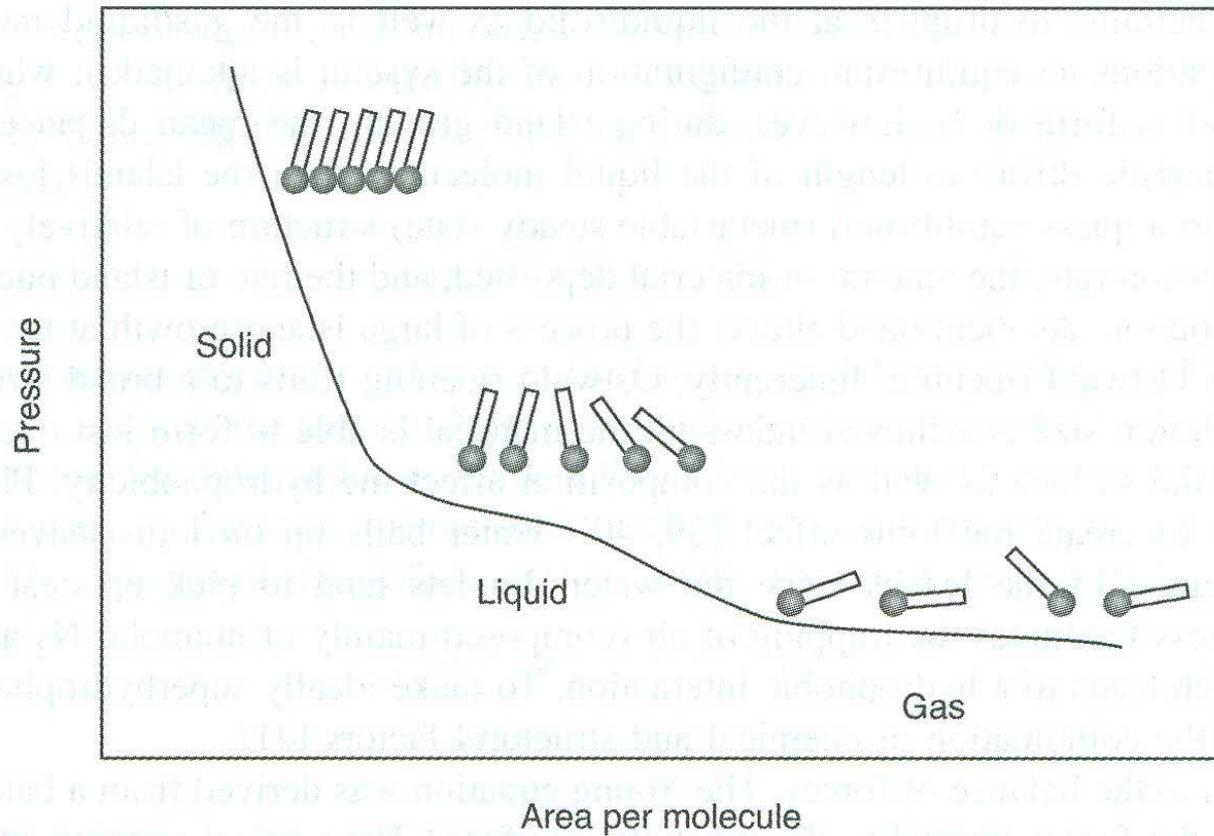• Surface pressure is exerted on the 2D barrier by a series of collisions
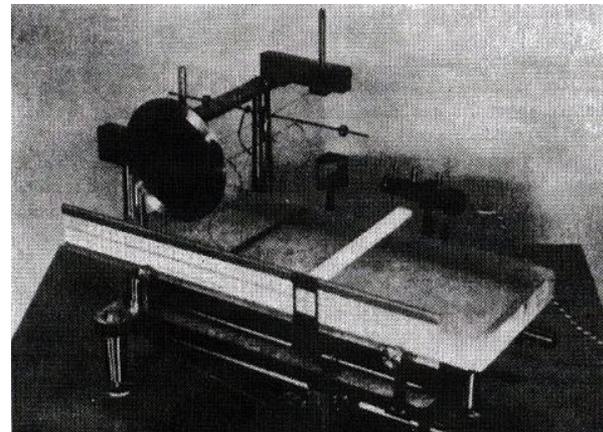
Figure 5.5 *Phase diagram of surface pressure versus area per molecule (amphiphile) in a Langmuir film. The (hydrophobic) tails should only be considered rigid in the solid-like phase in which tail–tail interactions lock them into an ordered structure.*

Gaseous films

• Molecules in a gaseous film behaves like a 2D gas.   Assume no lateral interaction

• Equation of state:

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

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

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

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

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

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

$$\pi A = kT$$

• 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.

•e.g.: 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.
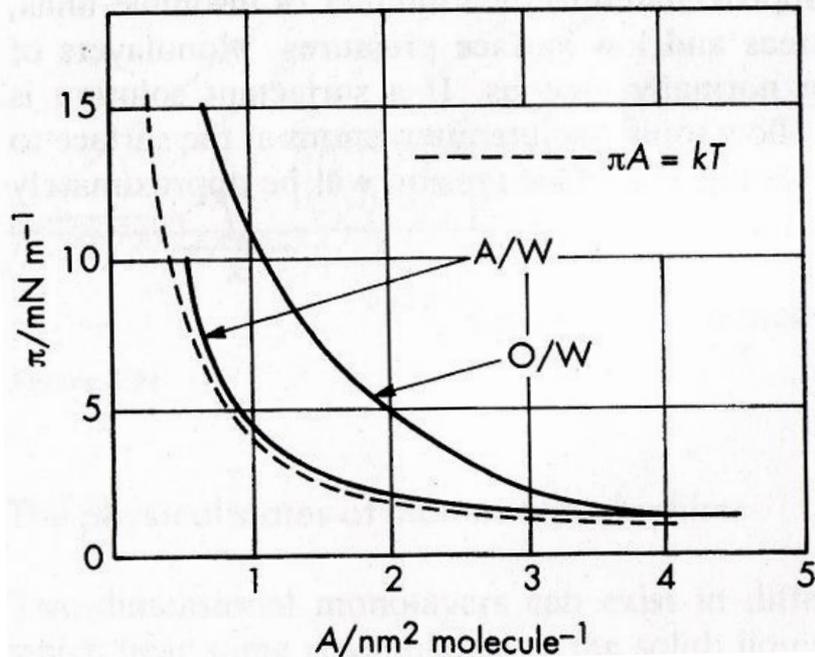
$\pi - A$ curves for CTAB at
Water-air and water-oil
Interfaces at 20 °C

Condensed films

- 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.
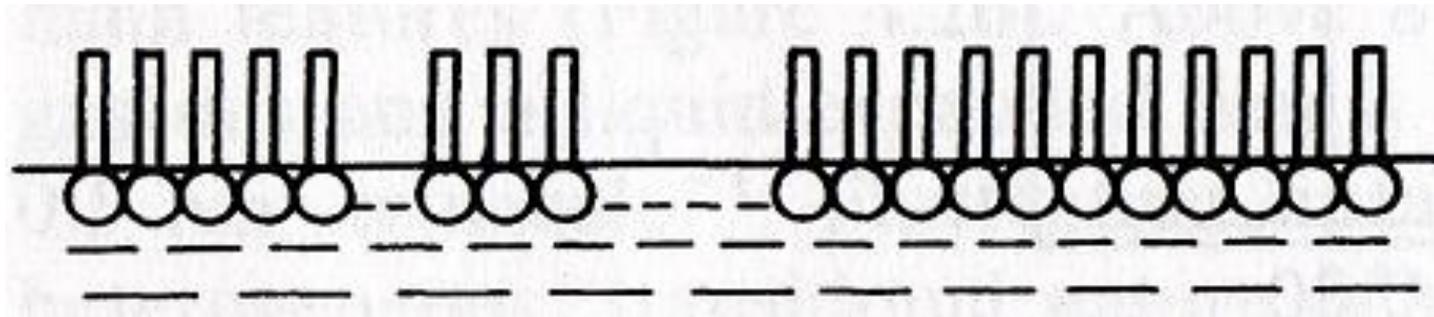

Fig. 4.23

- e.g.: $\pi - A$ 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 nm²** → initial packing of end groups.
- $\pi - A$ curve becomes very steep at **0.205 nm²** → more efficient packing by staggering and interlocking of the end groups.

- Limiting surface are = 0.20-0.22 nm² 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
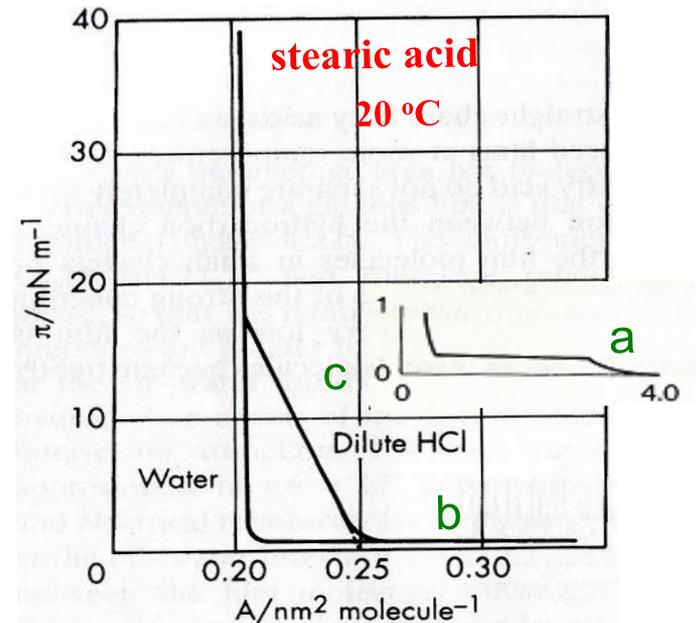- Further compression beyond this limit will eventually lead to collapse or buckling of the film.
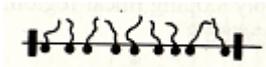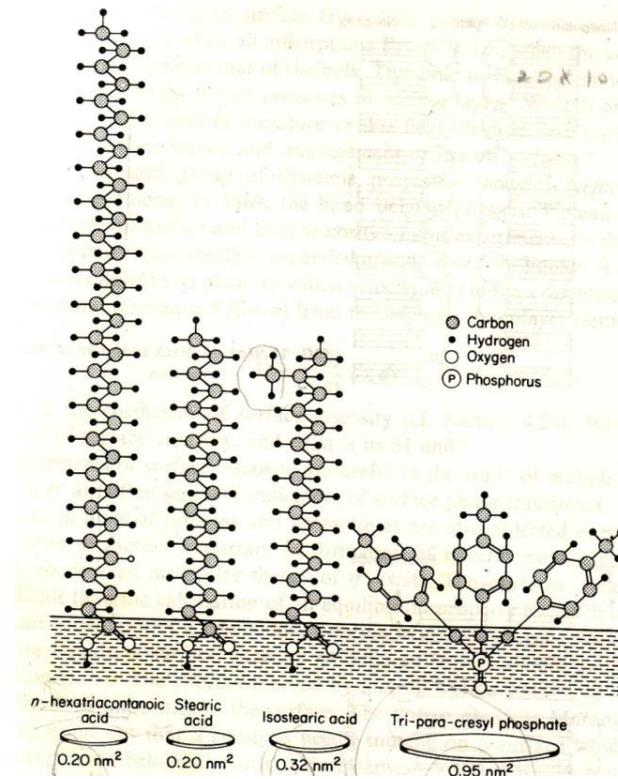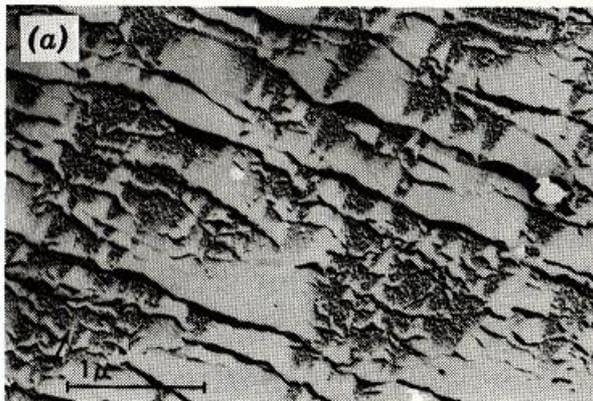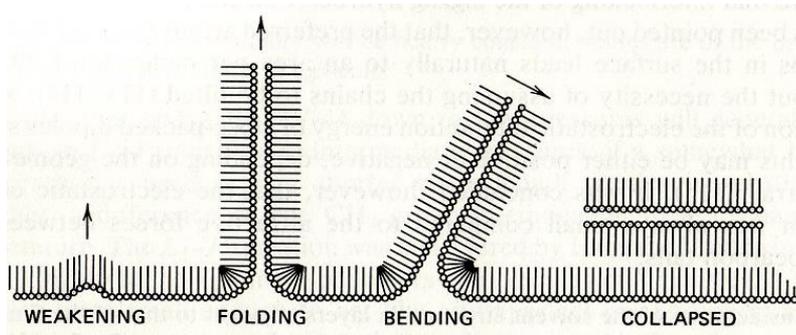
a) expanded   b) partially compressed   c) compressed

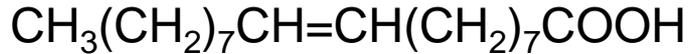
stearic acid 20 °C
π / mN m^{-1}
Dilute HCl
Water
A/nm² molecule^{-1}

Various forms of film deformation
beyond the elastic limit.

WEAKENING   FOLDING   BENDING   COLLAPSED

(a)

Carbon
Hydrogen
Oxygen
Phosphorus

n-hexatriacontanoic   Stearic
acid   acid   Isostearic acid   Tri-para-cresyl phosphate

0.20 nm²   0.20 nm²   0.32 nm²   0.95 nm²

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.
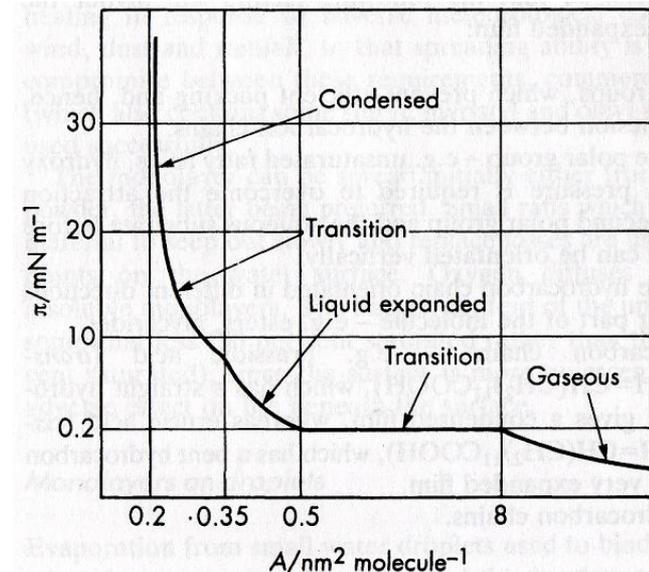• So π is larger for a given A .

van der Waals equation
$$(\pi - \pi_0)(A-A_0) = kT$$

• The $\pi - A$ 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.
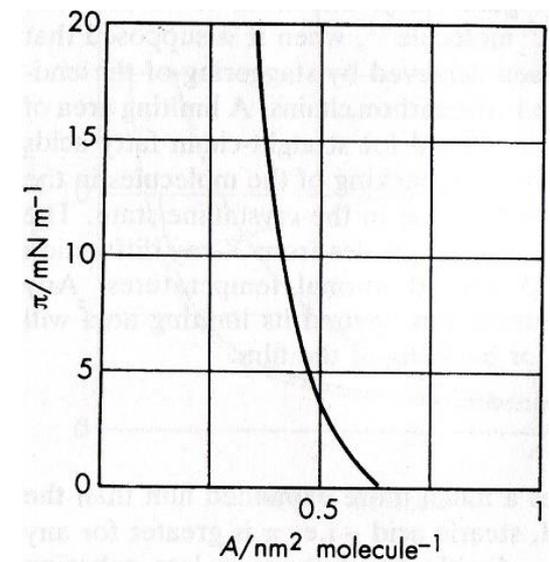

$\pi - A$ curve for oleicacid on water at 20 ºC

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℃ 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 direction 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: Ca^{2+} ions form insoluble calcium soaps with fatty acid films (unless the pH is very low), thus making the film more condensed.
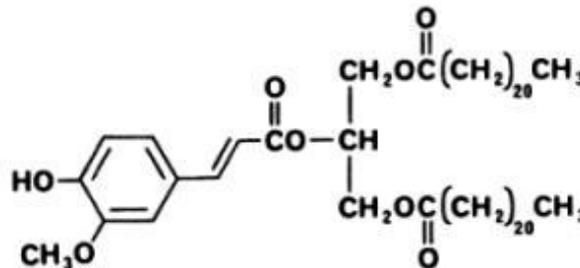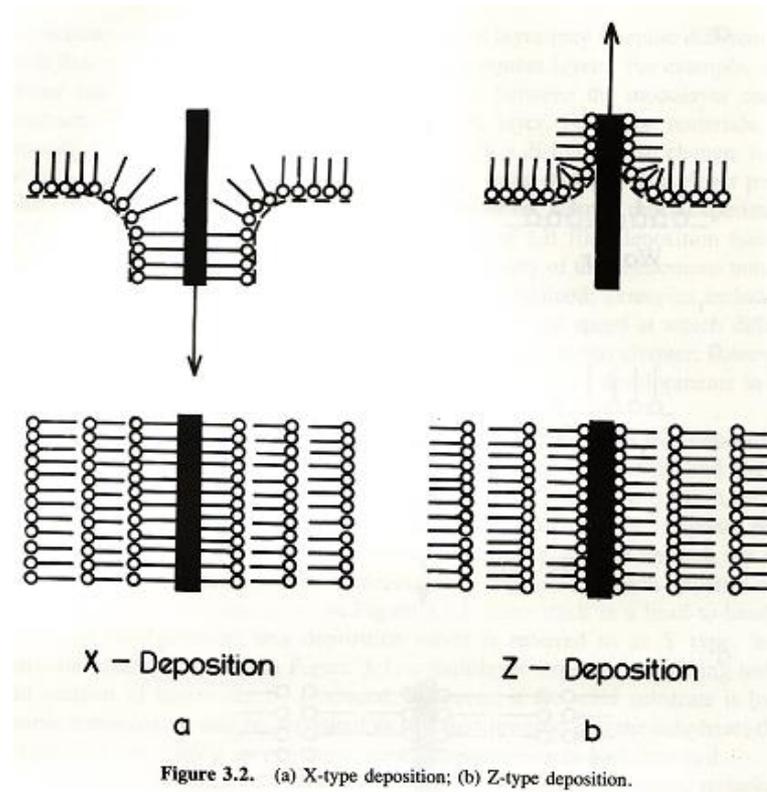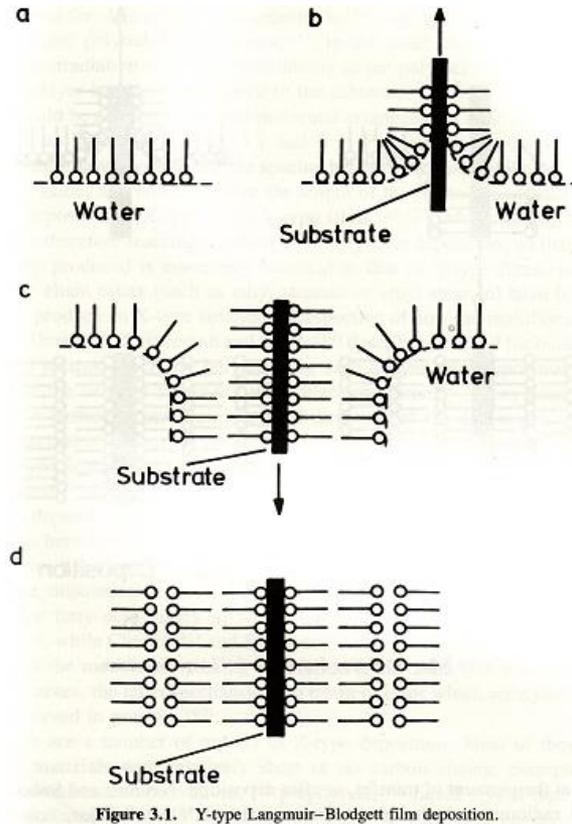

triiglyceride

Film deposition

Langmuir-Blodgett film   A film of amphiphiles transferred on to a solid surface

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

X – Deposition

Z – Deposition

a

b

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

Controlling parameters: pH, surface pressure etc.

Self assembled monolayers (SAMs)

Molecular assembles formed spontaneously by immersion of an appropriate substrate into a solution of an active surfactant in an organic solvent
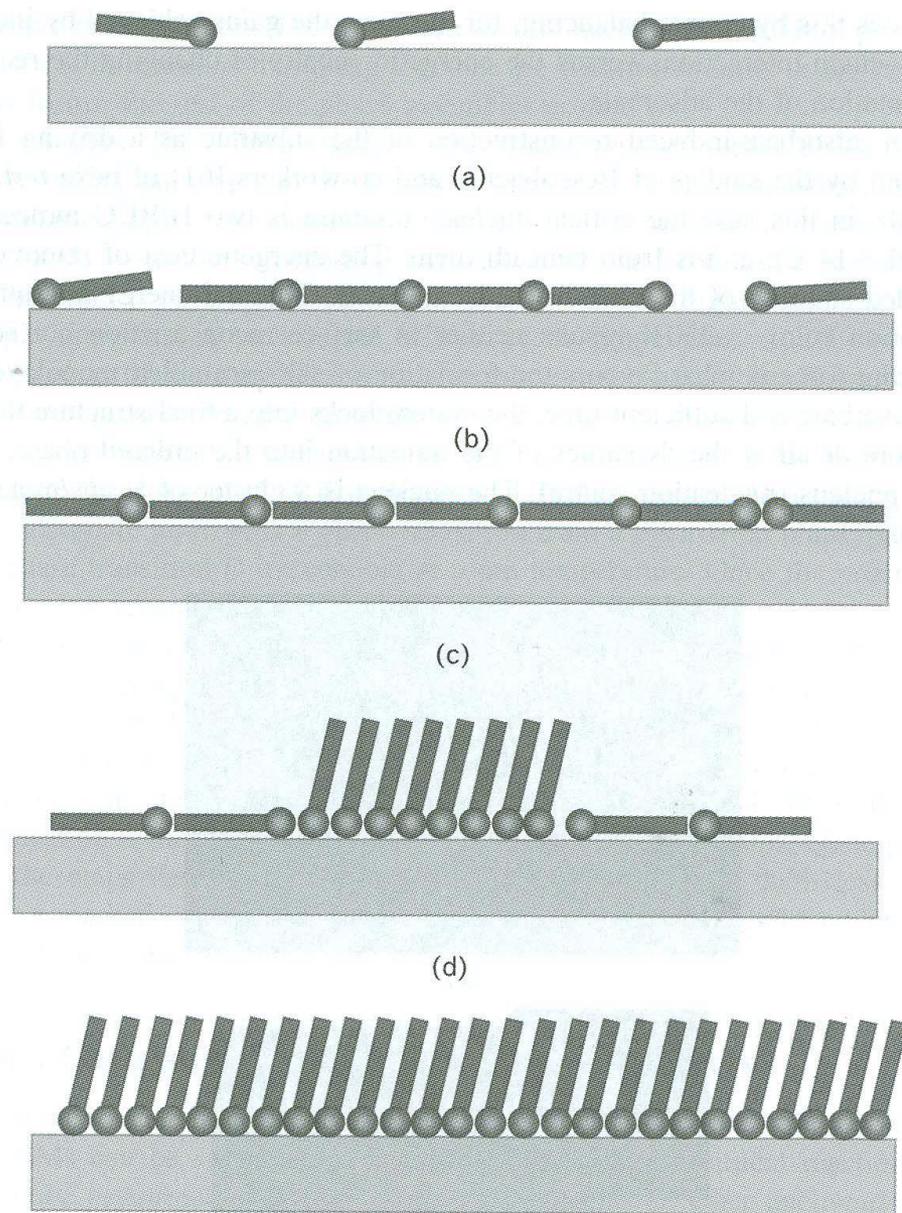

(a)

(b)

(c)

(d)

Figure 5.11 *Mechanism of self assembly: (a) disordered, mobile lattice gas; (b) lattice gas plus ordered islands; (c) saturated surface-aligned phase; (d) nucleation of solid-phase islands; (e) saturated solid phase. Self-assembly progresses in stages, as long as a sufficient supply of adsorbates is available, until the thermodynamically most favoured final state is reached. Not depicted in the figure is a reconstruction of the surface, which often accompanies the process.*