Chapter 8   Liquid-Liquid Interfaces

Distinct characteristics of liquids compared with solid and gas:

- Relative high density (than gas) and fixed volume
- Posses a mobility many order of magnitude greater than solids.----so, interface involving liquids generally behave as homogeneous.

8.1 The nature of a liquid surface: surface tension

Surface tension:

- An imbalance of the forces on surface molecules pulling into the bulk liquid and out into the adjoining vapor phase. Unit: force/length   (dyne/cm, mN/m)

- Surface energy: amount of work required to increase the surface area of the liquid by a unit amount. (unit: J/m^2, erg/cm^2)
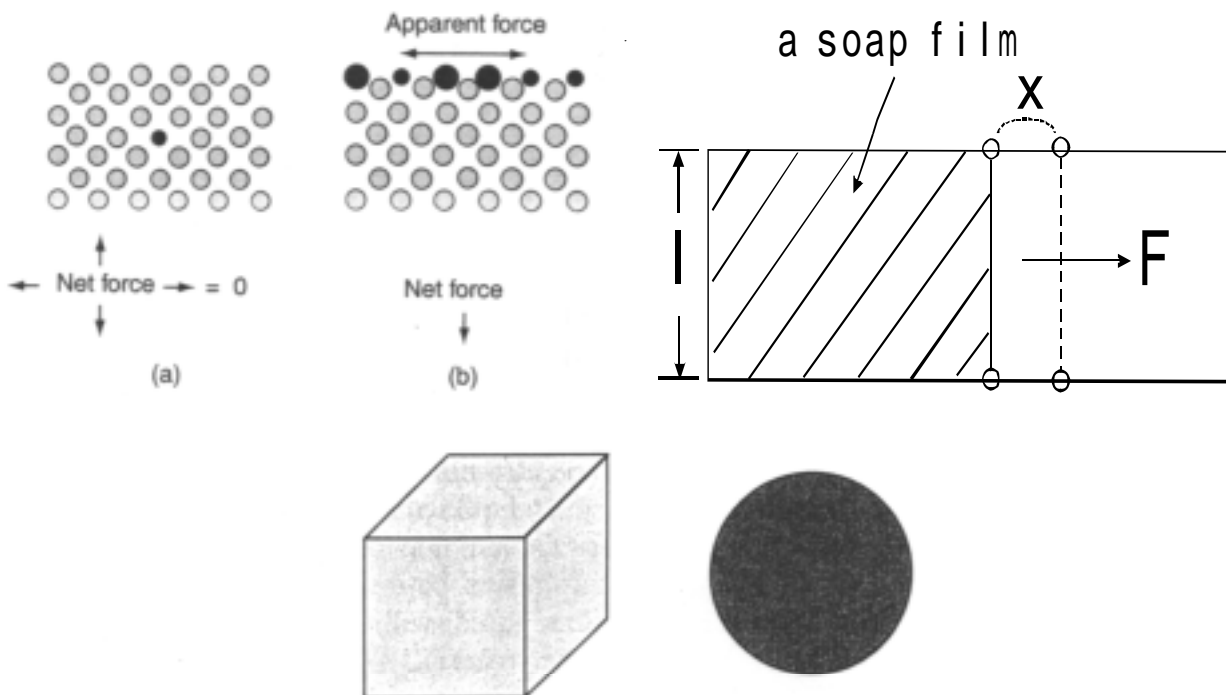

FIGURE 8.1. The unbalanced, inward pull of bulk liquid molecules on those at the surface results in the phenomenon observed as surface tension. The drive to reduce the surface area to a minimum produces the observed tendency of liquids to form spherical drops (in the absence of gravity)—the geometry of minimum surface area for a given volume of material.

- The various attractive interactions of the two phases across the interface:

  Liquid-gas > liquid-liquid,   so

  The interfacial tension (excess surface energy) in liquid-liquid system will be lower than in liquid-gas interface.

TABLE 8.1. Typical Liquid Surface and Interfacial Tensions at 20°C (mN m-1)

Liquid	Surface Tension	Interfacial Tension versus Water
Water	72.8	—
Ethanol	22.3	—
n-Octanol	27.5	8.5
Acetic acid	27.6	—
Oleic acid	32.5	7.0
Acetone	23.7	—
Carbon tetrachloride	26.8	45.1
Benzene	28.9	35.0 (357 vs. mercury)
n-Hexane	18.4	51.1 (378 vs. mercury)
n-Octane	21.8	50.8
Mercury	485	375

  Summary found in Table 8.1
- The surface tension of water (71-73 dyne/cm at room temp.) is larger than those of the organic solvent.
- The surface tension of organic solvent changes only slightly with the chain length (molecular weight).
- The interfacial tension between two liquids:
  (a). two liquids of highly immiscible---- $\sigma_{12} \approx |\sigma_{12} - \sigma_{12}|$
  (b) significantly miscible ----$\sigma_{12} \ll |\sigma_{12} - \sigma_{12}|$

8.1.1 Surface mobility

The surface or interface is commonly considered as static. In reality, rapid interchange of molecules between the bulk and interfacial region, and between the liquid and vapor phases should be existed. In equilibrium, the exchange rate, β is

$$\beta = \alpha \, (2\pi mkT)^{1/2} \, p_0 \qquad\qquad (8.1)$$

α : sticking coefficient (0.03 – 1.0)

p_0 : equilibrium vapor pressure of the liquid.

m: mass of the molecule.

The estimated residence time (25 ºC):

   Water: < 3 ms

   Mercury: ≈5 ms

   Tungsten: 10^{37} s

● With such molecular mobility, it is clear that the surface of pure liquid offers little resistance (compared with solid) to forces that may act to change its shape.

8.1.2 Temperature Effects on Surface Tension

● An increase in temperature → increase in surface mobility → increase the total entropy of the surface →reduce the free energy, ΔG, and reduce σ

$$\sigma = \Delta G/\Delta A$$

● At temperature near the critical temperature, T_c, of a liquid, the surface tension approached zero. (cohesive forces acting between molecules are very small, vapor cannot be condensed)

● Empirical equation to predict the temperature coefficient of surface tension (Ramsey and Shields):

$$\sigma \, (Mx/\rho)^{2/3} = k_s(T_c - T - 6) \qquad\qquad (8.3)$$

M: molar mass, *ρ*: density, *x*: degree of association, k_s: constant

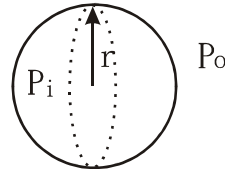## 8.1.3. The Effects of Surface Curvature

A pressure differential will be developed across any curved surface.

- Pressure difference, Δp, inside a bubble ($\Delta p = p_i - p_o$) ----
Young-Laplace equation:

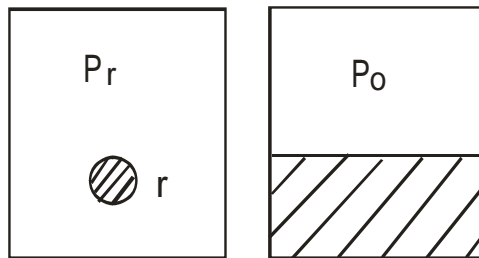$\Delta p = \sigma(1/r_1 + 1/r_2)$ (8.4)

When $r_1 = r_2 = r$ (sphere)

$\Delta p = 2\sigma/r$
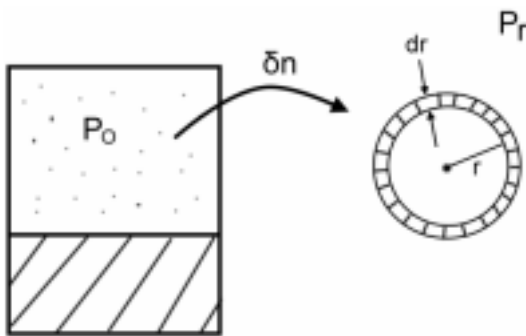
- For a very small drop of radius *r*, the vapor pressure (p_r) is higher than that over a flat surface (p_0).------ Kelvin equation

$RT \ln (p_r/p_0) = 2\sigma M/r\rho = 2\sigma V_m /r$ (8.6)

- For a drop of water with a radius of 1 nm, $p_r = 3p_0$

The condensation of liquid molecules to form very small drops will be retarded by a relatively high energy barrier due to the curvature.

$surface\ area\ increase: \ 8\pi r dr$

$surface\ energy\ increase: \ \sigma 8\pi r dr$

$\delta n\ moles\ \ from\ P_0 \rightarrow P_r$

$\Delta G = \delta n RT \ln \dfrac{P_r}{P_0}\ \ (= 8\pi r dr \cdot \sigma)$

$\delta n = (4\pi r^2 dr)/V_m$

8.1.4 Dynamic Surface Tension

● When new surface is created, it is reasonable to assume that a finite amount of time will be required for new molecules to diffuse to the surface and to return the system to equilibrium.

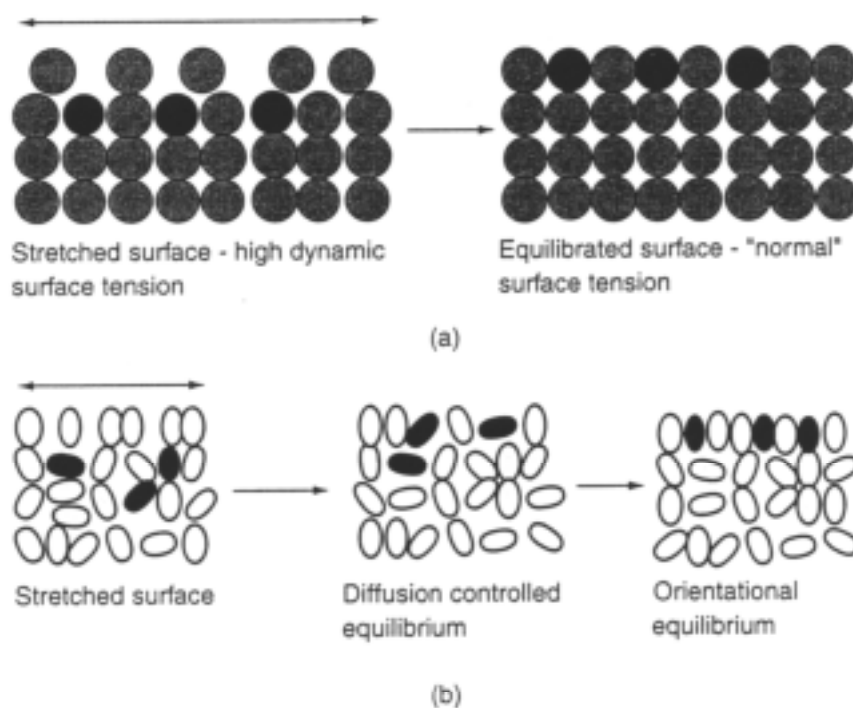■ The surface tension of such new surface is referred to the dynamic surface tension.

Stretched surface - high dynamic surface tension

Equilibrated surface - "normal" surface tension

(a)

Stretched surface

Diffusion controlled equilibrium

Orientational equilibrium

(b)

FIGURE 8.2. Dynamic surface tension in pure liquids: (*a*) for a liquid of isotropic molecular shape, dynamic surface tension effects are controlled by the rate of diffusion of molecules from the bulk to the new surface; (*b*) in polar or anisotropic liquids, the situation may be further complicated by the question of molecular orientation at the surface.

<u>Time required to attain equilibrium</u> after new surface is created---

- Time for diffusion of liquid molecules to the surface (self-diffusion constant, 10^{-6} cm^2/s), about milliseconds order--- difficult to measure surface tensions over such short time.

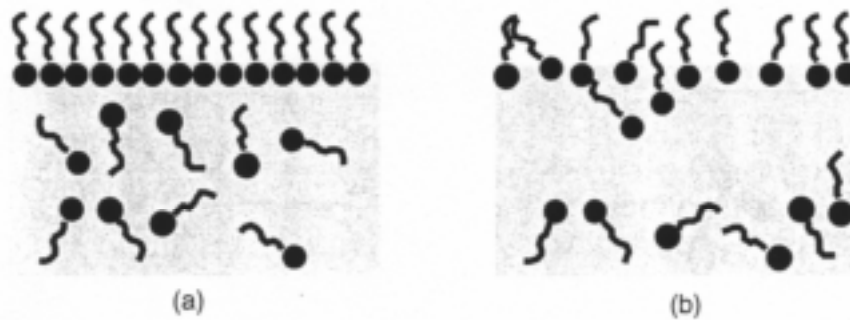 Low molecular weight, high bulk concentration → high diffusion rate

(a)   (b)

FIGURE 8.3. Dynamic surface tension effects can be particularly important in certain applications of surfactant solutions. (*a*) In a quiescent solution, the surface concentration and orientation of surfactant molecules produces the equilibrium surface tension. (*b*) When new surface is formed rapidly, as in certain coating operations, diffusion of surfactant molecules to the new surface from the bulk will require a certain time, reflected as a dynamic surface tension, greater than the equilibrium value. If significant new surface is formed, the concentration of surfactant near the surface may be depleted, producing a greater dynamic effect.

- Molecular orientation at the surface--- for asymmetric molecules (such as alcohols or surfactants), the surface tension will be a function of the orientation of the molecule at the interface. Some finite time is required for orientation to occur.

  - Polymer solutions may take minutes, hours, or even days to attain equilibrium due primarily to the long time required for the chain to orient.
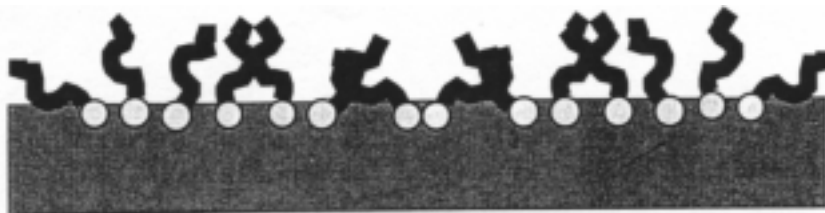

FIGURE 8.4. Polar molecules in solution will, when possible, orient themselves at surfaces and interfaces in order to minimize the overall interfacial energy of the system. In aqueous solutions containing organic solutes that usually results in the nonpolar portion of the molecule "pointing" away from the aqueous phase, or at least lying along the surface.

8.2 Surface Tensions of Solutions

The presence of solute often results in the alternation of surface tension. Most commonly, the effect is to lower the surface tensions, however, the opposite effect is also found.

● **For two miscible liquids**:

For an *ideal binary mixture*, the surface tension of the solution σ_{mix} :

$$\sigma_{mix} = \sigma_1 X + \sigma_2 (1-X) , \qquad \text{X: mole fraction of component 1}$$

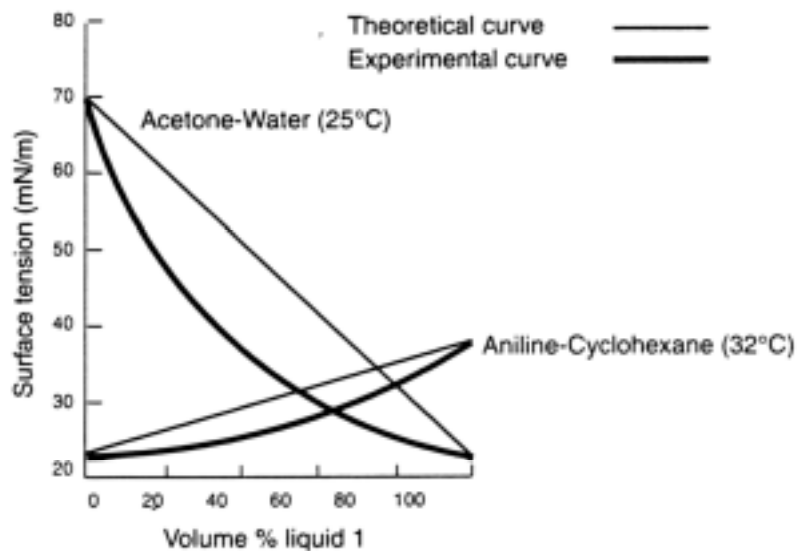■ Normally, there will be some *positive* of *negative* deviation from linearity. (Fig. 8.5)

FIGURE 8.5. For an ideal mixture, the surface tension will be a linear function of the composition of the mixture and the surface tension of the pure components (light lines). In practice, most mixtures show significant deviation from ideality (bold lines).

● **When the second component is an inorganic electrolyte**

The addition of inorganic electrolyte always results in an increase in the surface tension of the solution. (the effect is not dramatic and requires rather high salt concentration) ---- Fig. 8.6
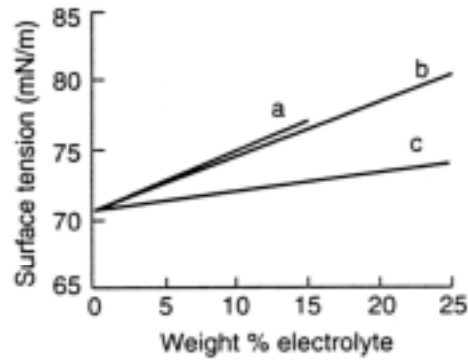
FIGURE 8.6. Unlike organic solutes, many common inorganic electrolytes can produce increases in the surface tension in aqueous solution, although relatively high concentrations are usually required to produce significant increases. Typical values include those for LiCl (curve *a*), NaCl (curve *b*), and NaBr (curve *c*).

- ■ The relative effectiveness of ions in increasing the surface tension of water generally follows the **Hofmeister** series:

  $Li^+ > Na^+ > K^+$ and $F^- > Cl^- > Br^- > I^-$

  - ◆ The effect results from a structuring of the water molecules at the surface due to salvation phenomenon.

- ● **The solute is an organic material in aqueous solution**

  The surface tension will *decrease* with addition of organic solute and the extent of such lowing depends on: (1) hydrophilic head, (2). hydrophobic tail, (3) the tendency of the material to adsorb at the air-water interface. ---- Fig. 8.7
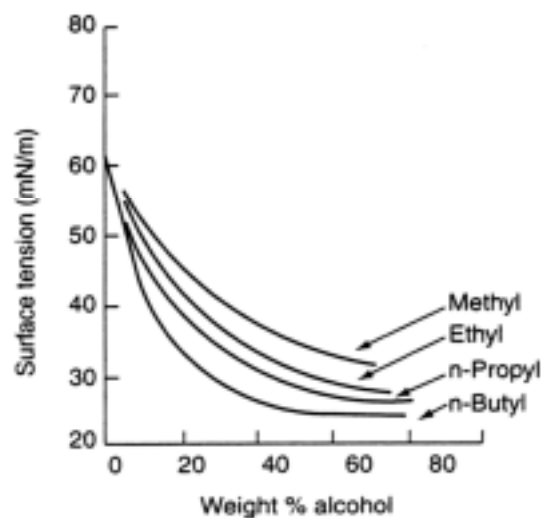

FIGURE 8.7. The effect of carbon number on the surface tension of water increases rapidly with the addition of each carbon unit, as illustrated for the series of short-chain alcohols.

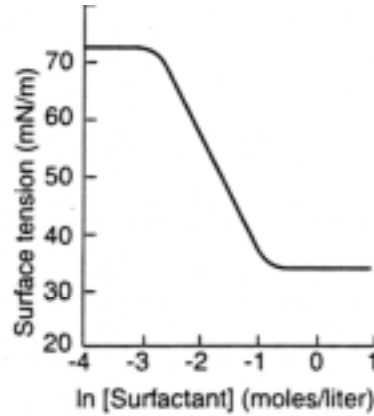■   Typical surface tension-concentration curve----Fig. 8.8

FIGURE 8.8. In a surfactant solution, the surface tension will typically change rapidly over a relatively small concentration range and then level off at some characteristic minimum value. The exact shape of the curve will depend on the molecular characteristics of the surfactant and its purity.

8.2.1. Surfactants and the Reduction of Surface Tension

Fundamental principle--- Gibbs adsorption equation

$$\Gamma_2 = -(1/RT)[d\sigma/d\ln c_2]$$

Surface tension of a liquid is determined by:

(1) Surface excess concentration,

(2) Surface activity of a surfactant molecules (K_L:Langmuir equilibrium adsorption constant))

The Szyszkowski equation of Langmuir isotherm:

$$\sigma = \sigma_0 - nRT\Gamma_m \ln(1 + K_L C)$$

8.2.2 Effect of phase Densities

If the **vapor phase** is replaced by a **condensed phase** that has a *higher molecular density and more opportunity for attractive interaction* between molecules in the interfacial region, the interfacial tension will be **reduced**.

Example: Octane-water--- (weak dispersion force): to 52 mN/m

Octanol-water – (polar group interact more specifically with water): to 8.5 mN/m

- Any alteration in the nature of the molecules composing the surface would be expected to result in lowing of surface energy of the system.---action of surfactant in lowing the surface tension.

- Most surfactants do not the affect the surface tension of organic liquid.

8.3 Surfactant Adsorption and Gibbs Monolayers

----- the basic concepts governing the adsorption of surface active molecules at the interface. –Gibbs adsorption isotherm.

8.3.1. Efficiency, Effectiveness, and Surfactant structure

- Two aspects of process used to discuss the performance of a surfactant

(1) *The concentration of surfactant in the bulk phase required to produce a given surface tension reduction-__surfactant efficiency__.*

Ex: the concentration required to reduce 20 mN/m of surfave tension, C_{20}.

(2) *The maximum reduction in surface tension that can be obtained –__surfactant effectiveness__.*

- Surfactant characteristic is relative to:

    (1). surfactant structure, (2). substitution of surfactant for solvent molecules at the interface.

A surfactant can be expressed as:

$$CH_3(CH_2)_n\text{-}S, \quad \text{S: hydrophilic head group}$$
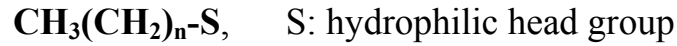
- The efficiency of a surfactant can be defined mathematically by the expression

$$-\log (C)_{20} = pC_{20} = n(-A)/2.3RT + (-B)/2.3RT + K \qquad (8.9)$$

A, B, *K*: terms for the free energies of transfer of methylene (CH_2), terminal methyl (CH_3), and head groups (S), respectively.

- Surfactant efficiency: directly related to the thermodynamics of chain transfer from bulk to interface.

- For a given head group, the efficiency is directly dependent on the length of the hydrocarbon chain.

- Chain modification →alter characteristic of surfactant (change in hydrophobic character)

- Branching in the hydrophobic group results in a reduction in the hydrophobicity of surfactant chain.

- Carbon atoms located on branch sites contribute approximately 2/3 as much to the character as one located in the main chain.

- A benzene ring usually contributes an effect equivalent to ≈ 3.5 methylene group.

- The methylene group lying between two polar groups contribute an effect equivalent to ≈ 1/2 of that located in the main body of the hydrophobe.

- Polyoxyethylene (POE) nonionic surfactants with an average of 7-30 OE units, exhibit adsorption efficiencies that follow an approximately linear relationship:

$$pC_{20} = A_{tr} + mB_{tr}$$

A_{tr}: constant related to $-CH2-$
B_{tr}: constant related to OE group,
m : number of OE units in POE chain

  - The efficiency of adsorption decreases slightly as m increases.

8.3.2 Adsorption Effectiveness

Related to the character of the maximum lowing of surface tension, (σ_{min}).

  - Approaches at maximum amount of surfactant adsorbed, Γ_m, which is reached at maximum bulk concentration of *free surfactant*.

  - (σ_{min}) will be determined by one of two factors:

    (a). solubility limit of Krafft temperature (T_k)----surfactant should be used above its T_k.

    (b) critical micelle concentration (CMC).

Typical relationship of σ vs. $\ln C$ →linear, for concentration below CMC

$$-\Delta\sigma_{cmc} = (\sigma_o - \sigma_1) + 2.3\ nRT\Gamma_m log(C_{cmc}/C_1) \qquad (8.11)$$

- A usuful method to evaluate surfactant effectiveness is by C_{cmc}/C_{20}

  - A *large value* of C_{cmc}/C_{20} indicates that the available free surfactant is being used *more effectively*.---Table 8.2

TABLE 8.2. Experimental Values of cmc/C_{20}, G20 ($\times 10^{10}$ mol cm^{-2}), and σ_{min} (mN m^{-1}) for Some Typical Surfactants in Aqueous Solution

Surfactant	Temperature (°C)	cmc/C_{20}	Γ_{20}	σ_{min}
$C_{12}H_{25}SO_4^-Na^+$	25	2.0	3.3	40.3
$C_{12}H_{25}SO_3^-Na^+$	25	2.3	2.9	40.8
$C_{16}H_{33}SO_4^-Na^+$	60	2.5	3.3	37.8
$C_{12}H_{25}C_6H_4SO_3^-Na^+$	70	1.3	3.7	47.0
$C_{12}H_{25}C_5H_5N^+Br^-$	30	2.1	2.8	42.8
$C_{14}H_{29}C_5H_5N^+Br^-$	30	2.2	2.8	41.8
$C_{12}H_{25}N(CH_3)_3^+Br^-$	30	2.1	2.7	41.8
$C_{10}H_{21}(POE)_6OH$	25	17.0	3.0	30.8
$C_{12}H_{25}(POE)_6OH$	25	9.6	3.7	31.8
$C_{16}H_{33}(POE)_6OH$	25	6.3	4.4	32.8
$C_{12}H_{25}(POE)_9OH$	23	17.0	2.3	36.8
$C_{16}H_{33}(POE)_9OH$	25	7.8	3.1	36.8
$C_{12}H_{25}(POE)_{12}OH$	23	11.8	1.9	40.8
$C_{16}H_{33}(POE)_{12}OH$	25	8.5	2.3	39.8
$C_{16}H_{33}(POE)_{15}OH$	25	8.9	2.1	40.8

■ The *efficiency* and *effectiveness* of surfactants may not run parallel.--- It is commonly observed that the materials that produce significant lowering of the surface tension at low concentrations (i.e., are more efficient) are less effectiveness (i.e., have a smaller Γ_m)
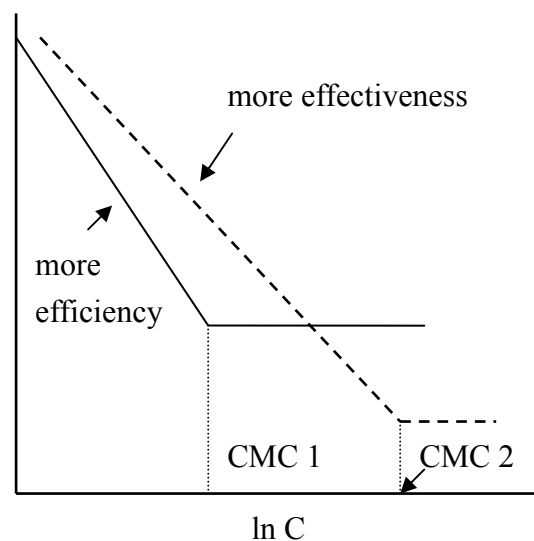
- The role of molecular structure in effectiveness is directed related to the size of the adsorbed molecules.----either hydrophobic or hydrophilic portions
  - Maximum number of molecules that can be fitted into a given area (Γ_m) depends on the *cross-sectional area* of the **hydrophobic chain** or of the **head group**, whichever is greater. (Fig. 8.9)
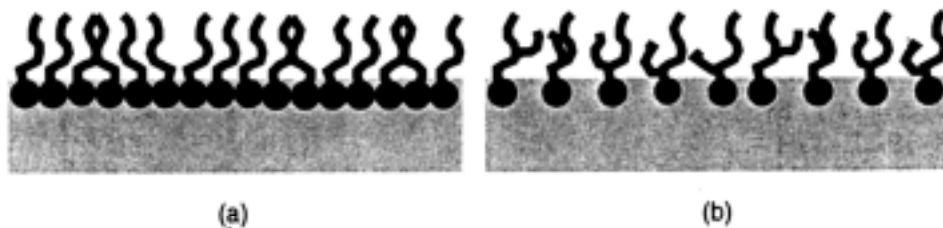

FIGURE 8.9. The packing efficiency of a surfactant at the surface will be determined by the combined effects of the hydrophilic head group and the hydrophobic tail: (*a*) straight chains and large head groups (relative to the tail cross section) favor close, effective packing; (*b*) branched, bulky, or multiple hydrophobic chains hinder effective close packing at the interface.

-
  - For straight chain ionic surfactant→the head group is always predominated.-----so, A_{min} varies only slightly with the length of the hydrocarbon chain.(Table 8.2)
  - A_{min} relate to Γ_m, Γ_m increases → A_{min} decreases (higher effectiveness)
  - The sign of the charge on the ionic surfactant has only minor effect------indicating that geometric requirement are fairly constant from one head group to the next.
  - In the presence of electrolyte→electrostatic repulsion between adjacent molecules are reduced →effective area becomes smaller →slight increase in surfactant effectiveness.
  - For normal alkyl surfactants, chain lengths $C_8 - C_{20}$ have minor effect on the effectiveness.
- Other structure changes that give much more dramatic effects:
  - Branching and multiple-chain hydrophobe →increases in CMC→increase in effectiveness (smaller effect on efficiency)

- Introduction of another polar groups located well away from the head group (Fig. 8.10) →change in orientation of the adsorbed molecules →significant lowing of both efficiency and effectiveness.

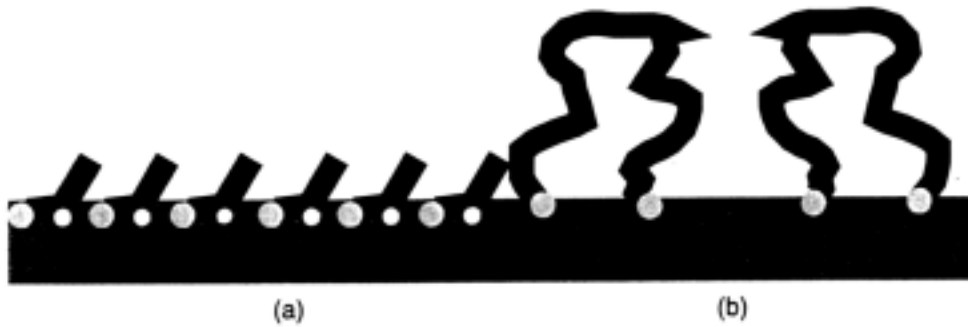(a)   (b)

FIGURE 8.10. The presence of a second polar group near the principle hydrophile, or further along the chain, will affect the surface area occupied by each surfactant molecule and, therefore, its surface characteristics.

- When *fluorine* atoms are substituted for hydrogen in the hydrophobic group →significant increase in the efficiency and effectiveness
  - fluorinated organic materials have a little interaction with adjacent phase→high driving force for adsorption→high efficiency
  - fluorine has very low surface energy →very low surface tension (high effectiveness)
- Effects of counterion: tight ion bounding reduces the electrostatic repulsion between adsorbed molecules →tighter packing of surfactant → increases in both the efficiency and the effectiveness.
- The head group may be of minor importance for hydrophiles closely related in size and charge character.

    Ex: $R\text{-}N^+(CH_3)_3X^-$ (cationic surfactant)

  - The substitution of larger alkyl groups for methyl groups results in significantly reduction in efficiency of adsorption, while not affecting σ_{min} significantly.

8.4 Insoluble Monomolecular Films

Insoluble monolayer: for materials that have very low solubility in the supporting liquid phase and are essentially isolated on the surface.

A **schematic** comparison of the *adsorbed monolayer* (Gibbs monolayer) and the *insoluble monolayer* (Langmuir monolayer)--- Fig. 8.11
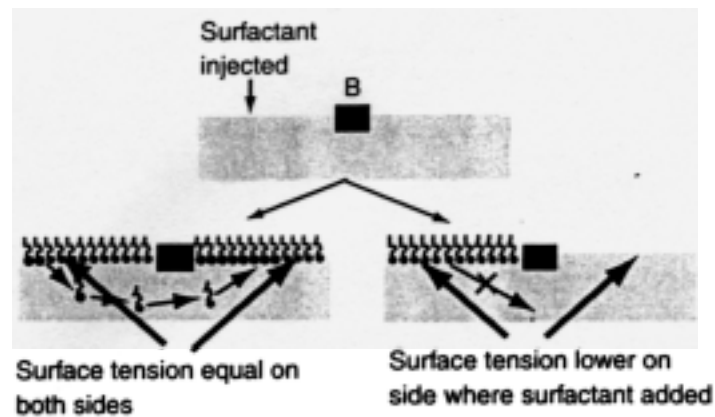

FIGURE 8.11. If a surface-active material is added to the surface of water in a container where the surface is divided by a barrier, two types of adsorption may occur: (*a*) if the material has significant solubility in water, diffusion through the water will occur and adsorption will result on both sides of the barrier to produce a Gibbs monolayer; (*b*) if the material is essentially insoluble in water, adsorption will occur on the side of the barrier to which it is applied, but not on the opposite side, leaving an insoluble monolayer.
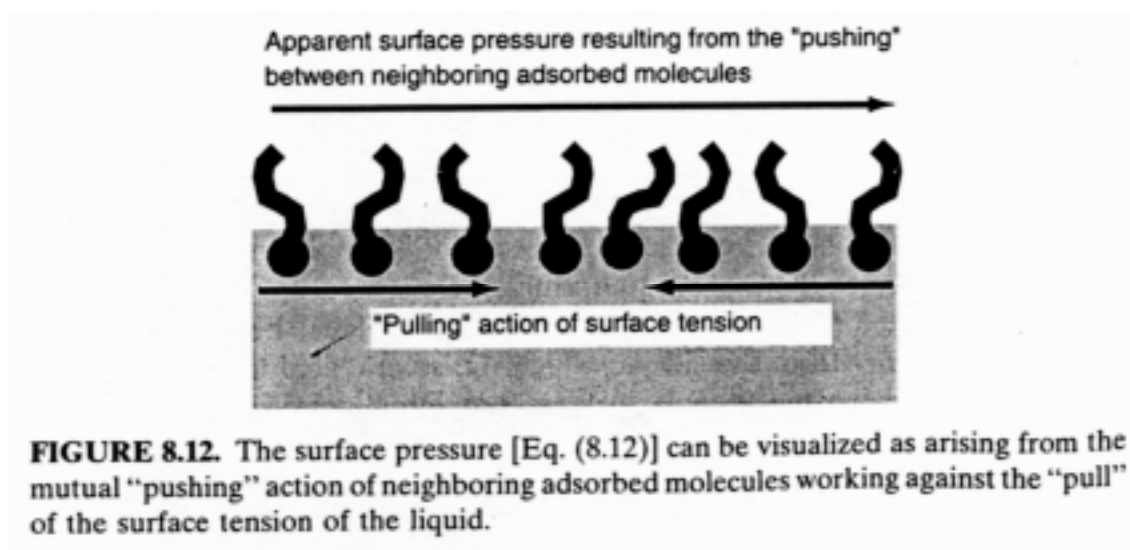
- If surfactant is injected to one side of the surface (as shown in Fig. 8.11) and wait for equilibrium.

  - For the left figure (Gibbs monolayer), $\sigma_L = \sigma_R$, the barrier B does not move

  - For the right figure (insoluble monolayer), the barrier will move away from the side to which the surfactant (stearic acid) is added.---- due to higher surface pressure.

8.4.1 Surface pressure (π)

$$\pi = \sigma_0 - \sigma$$

σ_0 : surface tension of the pure supporting liquid

physical meaning: the expanding pressure exerted by the neighboring molecules of monolayer against the surface tension (contracting) of the pure liquid subphase. (Fig. 8.12)

FIGURE 8.12. The surface pressure [Eq. (8.12)] can be visualized as arising from the mutual "pushing" action of neighboring adsorbed molecules working against the "pull" of the surface tension of the liquid.

● The pressure-area (π-A) curve can be constructed by compression the area of monolayer which allows one to determined about the nature of the film and some molecular characteristics of the adsorbed material

8.4.2 Surface Potential

Almost all surface-active materials have a polar head group. The dipole moments of these groups are partially orientated with respected to the interface when the molecules adsorb at the interface. As a result, the potential difference across the interface will be altered.

The surface potential, ΔV, is the change in the interfacial potential due to the presence of the monolayer.

- The measured surface film potential can be used to deduce information about the orientation of the adsorbed molecules. (but is only approximately)

$$\Delta V = n\ \mu\ \cos\theta/\varepsilon \qquad\qquad (8.13)$$

n: number of molecules in the films (known quantity)

μ: dipole moment of the head group (known or accessible)

ε: permittivity of the film (dielectric constant x permittivity of a vacuum)

- Eq (8.13) allows one to estimate the angle of inclination (θ) of the dipole to the surface normal → deduce the orientation of the entire molecules.

- For a *mixed monolayer*, the surface film potential can be used to estimate the homogeneity of the film, or the film composition (when the values of the pure films are known)

- Can be used to study the penetration of insoluble monolayer by materials injected just below the surface .(ex: monolayer: biological membrane, penetration material below film: drug)

8.4.3 Surface Rheology

In the presence of an adsorbed monolayer film (the Gibbs monolayer or Langmuir monolayer), the **rheological properties** (*surface viscosity, elasticity*) of the surface can be change.

- With increasing density of monolayer, the mobility of the film decreases. ----surface viscosity increases substantially and the film behaves as if it is in a condensed state.

- Increase in surface viscosity produced by adsorbed film → persistent forms, stabilize emulsion, dampening surface waves.

8.5 The Physical States of Monolayer Films

Characteristics of monolayer films can be distinguished as: gaseous, liquid, and solid states:
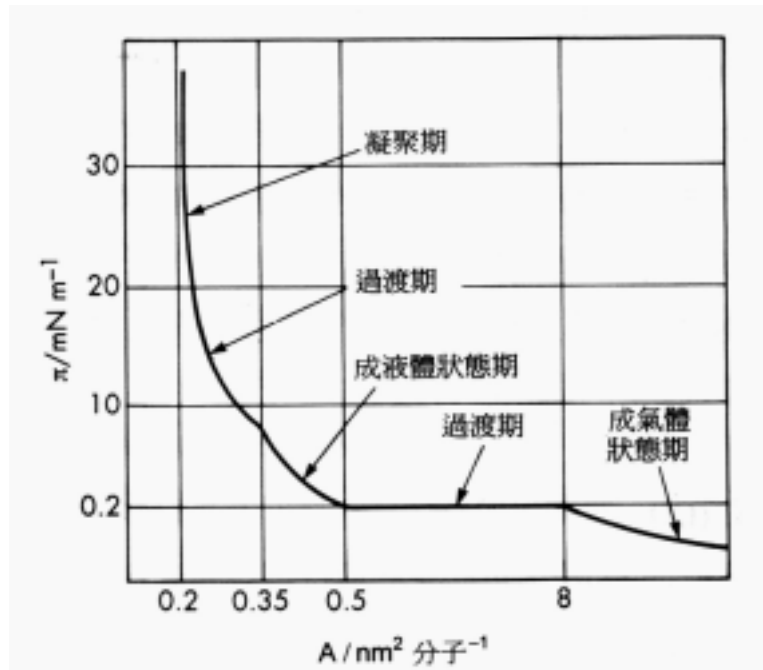
1. *Gaseous films*: the molecules are relatively far apart and have significant surface mobility, the molecules act essentially independently with random orientation, compressible.

2. *Liquid (expanded) film*: equivalent to the liquid state, molecules are coherent and densely packed, with much lower compressibility and more regular orientation than gaseous phase, approximately perpendicular to the surface but the tail are less rigidly packed.

3. *Condensed (solid) films*: molecules are coherent, rigid, incompressible, densely packed, with high surface viscosity and little mobility, oriented perpendicular to the surface.
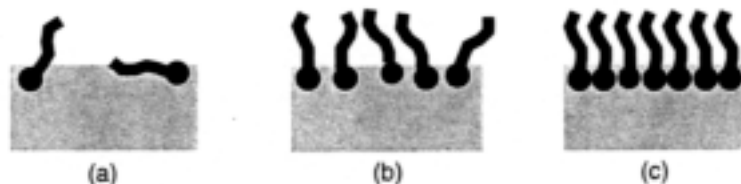

FIGURE 8.13. Molecules in a monomolecular film are usually considered to exist in one of three principle "states." (*a*) The gaseous state is that in which the molecules are relatively far apart and have little mutual interaction; the film is compressible. (*b*) The liquid expanded state is that in which the head groups are relatively closely packed, but there is significant degree of tail mobility; the film is compressible to a limited extent. (*c*) The condensed state in which the molecules are closely packed and have very limited mobility; the film is essentially incompressible.

8.5.1. Gaseous Films

An ideal (bulk) gas will have an equation of state given by the ideal gas law

$$PV = nRT \qquad (8.14)$$

Similarly, an "ideal" gaseous monolayer should follow the corresponding law

$$\pi A = kT \qquad (8.15)$$

which means that the π–A curve should be a rectangular parabola such as that in Figure 8.14. In fact, such ideal behavior is rare due to the finite size of the adsorbed molecules.
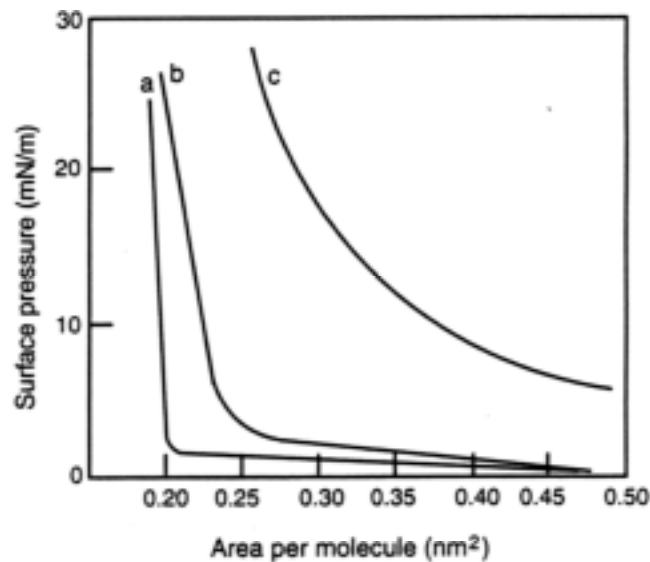

FIGURE 8.14. Each "state" of monomolecular films has a characteristic pressure–area (π–A) curve that can be used as a diagnostic tool for identifying the state of a given film: (a) the condensed film, being incompressible, has a sharp transition as the film area is decreased; (b) the liquid expanded film shows a more gradual transition as it is compressed, but the degree of compression is limited; (c) the gaseous film is relatively easy to compress and shows no sharp transition.

● Consider the molecular interactions:

$$\pi A = x\,k\,T \qquad (8.16)$$

x: constant (between 1 and 2) to adjust the interaction between molecules. (inconvenient to use)

- Modification by employing a constant $\underline{A_o}$ (area occupied by adsorbed molecule:

$$\Pi(A-Ao) = k\,T \qquad\qquad (8.17)$$

Ao: directly related to the cross-sectional area of the vertically adsorbed area. Alter by the interaction between molecules

- Combination of Eqs. (8.16) and (8.17)

$$\Pi(A-Ao) = x\,k\,T$$

8.5.2 Liquid Films

Liquid phase can be divided into two subclasses:

(1). *Liquid expanded (L_1)*: range between *gas* and *liquid condensed*

◆ exhibits a significant degree of compressibility, maintain uniform phase.

◆ For hydrocarbon alkyl chain, the limiting area is about 0.5 nm^2. (theoretical value $\approx 0.2\ nm^2$)

(2). Liquid condensed (L_2):

◆ has lower compressibility than L_1

◆ the π-A curve undergoes a gradual transition to linearity

◆ the head groups are closed packed, but can further be compressed to give a still tighter packing arrangement.--- (Fig. 8.15--- from cubic to hexagonal structure.)

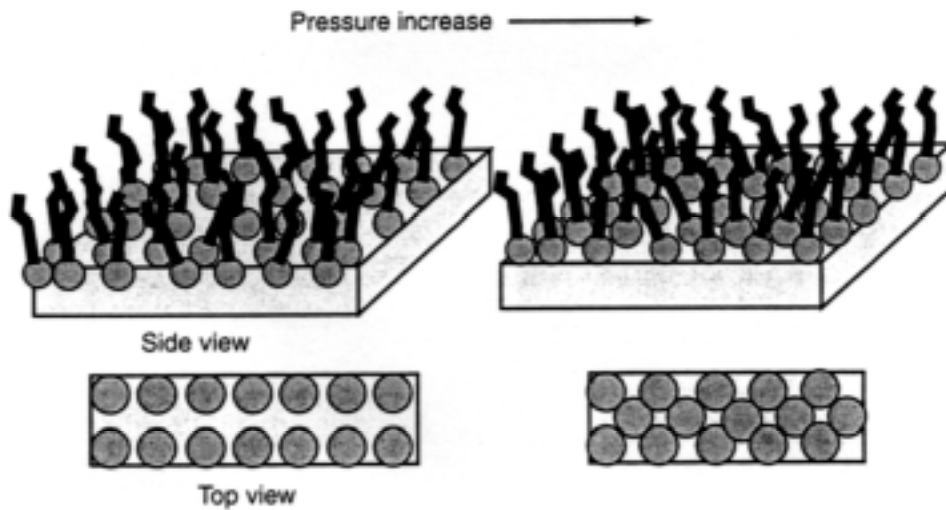◆ usually 10-20% larger than the cross-sectional area of hydrocarbon chain

FIGURE 8.15. As pressure is applied to a condensed film, the adsorbed molecules can rearrange to a small extent by a change in packing structure (e.g., cubic to hexagonal). Beyond that point added pressure will result in film "buckling."
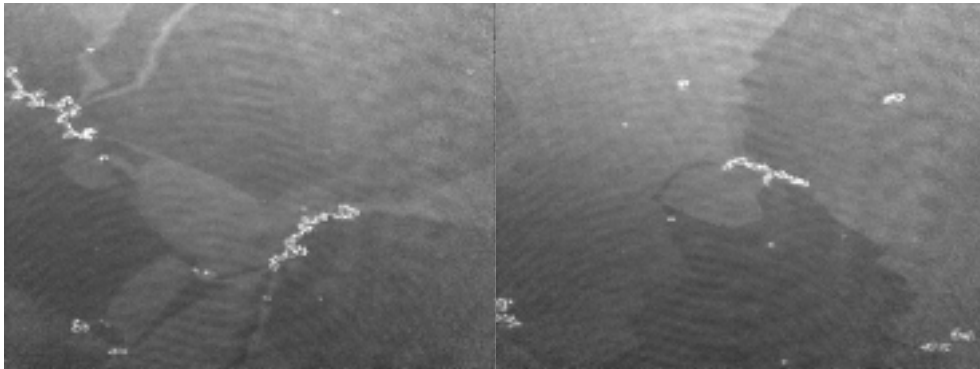
8.5.3. Condensed Films

● The cohesive interaction between molecules is sufficient to formation of clusters, the inter-clusters interaction is small

  ■ BAM images of stearic acid at gas phases ($\pi \approx 0$)
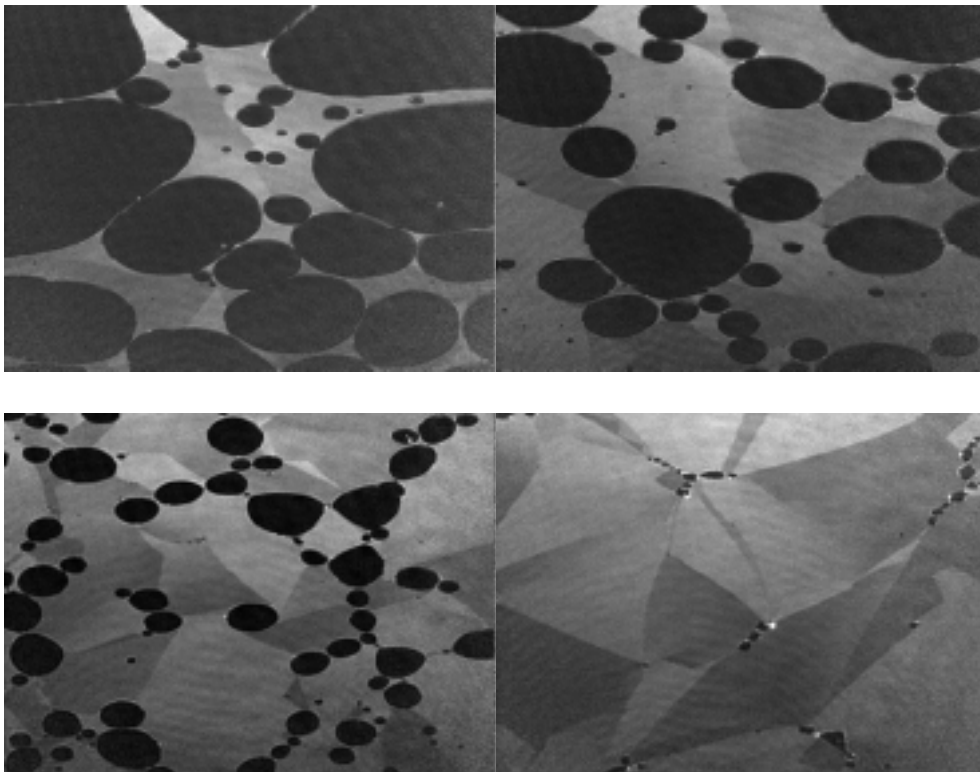
$\pi \approx 5$ (A=24.1) $\pi \approx 10$ (A≈23.1)

$\pi \approx 20$ (A≈ 21) $\pi \approx 30$ (A≈20.5)

- When the area is decreased to the point that the clusters are forced to interact by physical contact, the pressure increases rapidly.
- Typical π-A curve for stearic acid on water and HCl at 20 ^{o}C (Fig. 8.16)
    - ***On water***, the phase passes from gaseous to solid condensed phase without passing through the liquid expanded state.
    - ***On HCl*** (0.1N), the intermediate phase transitions occurring before the formation of condensed phase.
    - The critical molecular area for stearic acid is about **0.205 nm^2**, as well as that for palmitic and myristic, and other members of the series with more than 12 carbon.
    - The cross-sectional area of SA estimated by X-ray diffraction is about **0.185 nm^2**.
    - At state of condensed film, when the area is decreased further, the pressure suddenly falls. That point is commonly referred as **collapse point (yield point)**
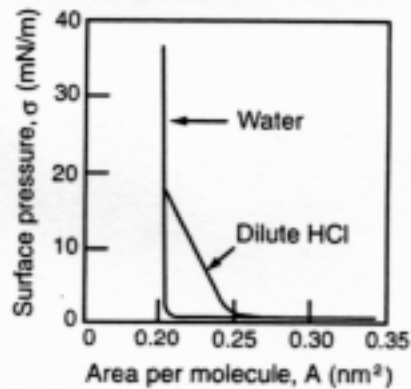
FIGURE 8.16. A monomolecular film of a straight chain carboxylic acid such as myristic acid on distilled water will show a sharp transition in the π–A curve as the head groups become more closely packed. That kind of transition may be viewed as something like a reversed sublimation in which the film passes from gaseous to solid condensed without passing through the liquid expanded state. With very careful experimental work, it is sometimes possible to identify an intermediate liquid expanded phase as illustrated for myristic acid on 0.1 N HCl.

8.5.4 Some Factors Affecting the Type of Film Formed

The types of monolayer film will depend on a number of factors: nature of tails and head group, degree of salvation of the head group, the supporting liquid phase, the temperature.

<u>The nature of the tail</u>.

- For straight-chain materials, ex. <u>Carboxylic acid</u> $(CH_3(CH_2)_nCOOH)$ --- Solid or L_2 film will be favored

   - Long chain length (e,g., $n \geq 14$) → solid film

   - Shorter chain length (e,g., $10 < n < 14$) → L_2 film

   - For $n < 8$ → gaseous film due to significant water solubility.

   - If the head group has higher solvation, (e.g., -OH of alcohol, $C_{18}OH$), can be compressed to L_2 film but not to solid film. But –COOH groups are much more strongly associated by themselves and produce a condensed film.

■ If the tail is branched or has two or more hydrocarbon chains (esters for example): the cross-sectional area becomes larger and formation of more expanded film.

■ For molecules containing two hydrophilic groups: interaction between molecules and water increases due to the second hydrophilic group → molecules tends to lie more flat on the water surface *at low surface pressure.*

As the pressure increases, energy is required to force those groups away from the surface → π will be greater. The process of standing up the tails in such a material is gradual, so that, a curve characteristic of an expanded film will result. (Fig. 8.17)
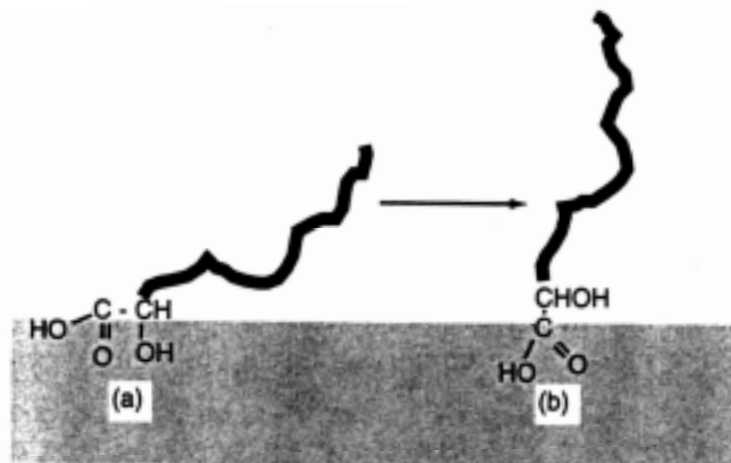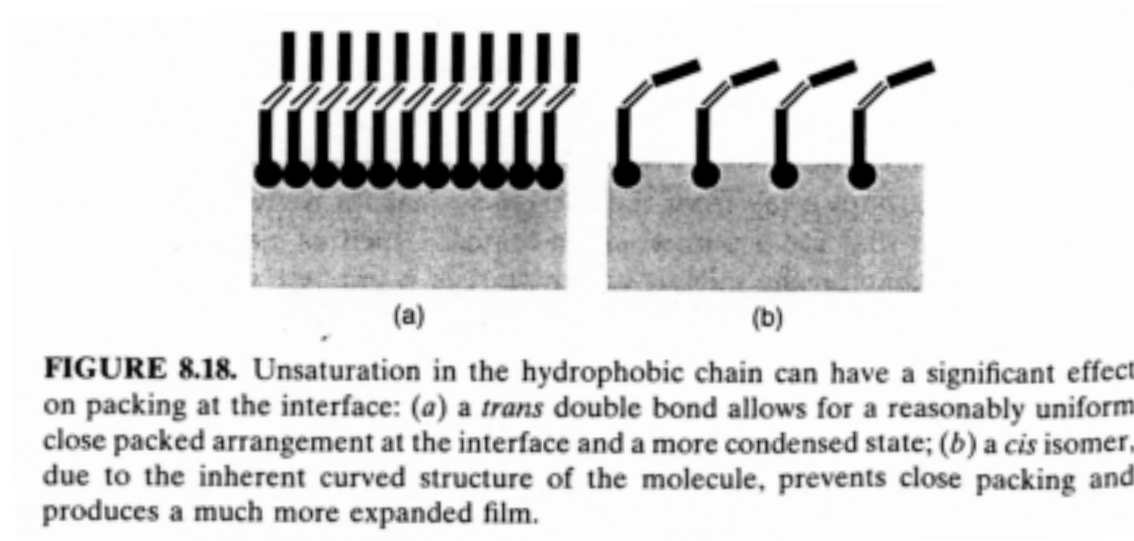

FIGURE 8.17. Surfactant molecules having two or more hydrophilic head groups will tend to lie more or less parallel to the liquid surface (*a*). As pressure is applied to the film, the molecules may be forced to "stand up" and assume a more vertical orientation (*b*). The energy requirements for such a process produces a π–A curve characteristic of a liquid-expanded film.

■ If <u>hydrogen</u> atoms are substituted by <u>fluorine</u> (or other halides): film type change from **solid** to L_2, due to packing difficulties imparted by bulkier halogen atoms as well as weaker cohesive interactions.

■ For unsaturated carboxylic acids:

(1). **Trans** double bond --- hydrocarbon chain will be more straight → high lateral interactions and good packing efficiency → solid or L_2 film.

(2). the **cis** isomer: has a forced bend structure, reducing the ability to pack tightly → expanded (L_1) film.   (Fig. 8.18)

FIGURE 8.18. Unsaturation in the hydrophobic chain can have a significant effect on packing at the interface: (*a*) a *trans* double bond allows for a reasonably uniform close packed arrangement at the interface and a more condensed state; (*b*) a *cis* isomer, due to the inherent curved structure of the molecule, prevents close packing and produces a much more expanded film.

Effect of Head Group.

● A bulky head group tends to keep the tails farther apart and prevent the packing efficiency. Form **expanded** rather than **solid** film.

● Charged head groups, the electrostatic repulsion between adjacent molecules force them apart and reduce interactions. →expanded film.

● Head group with high solubility (-OH for example), form more expanded films.

Effect of Temperature.

- Monolayer phases and phase changes are sensitive to temperature.

- As temperature is decreased: the monolayer goes from *expanded* to *condensed or solid*. (transition temperature)

- The transition temperature depends on the chain length (for the same head group). When addition of one $-CH_2-$ group, the transition temperature increases 5 °C.

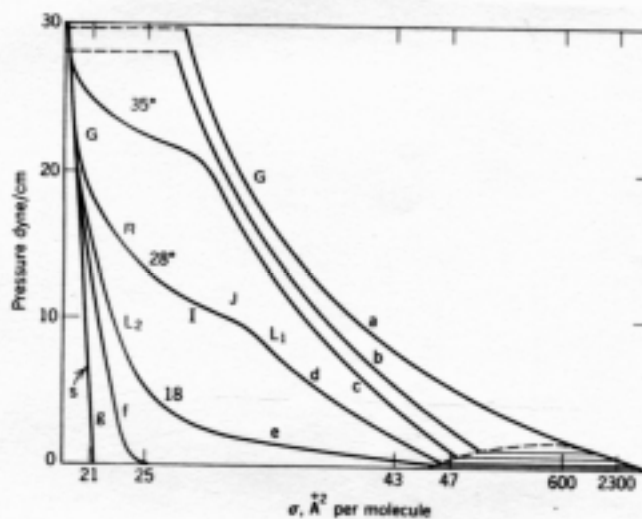- Typical figures showing the variation of isotherm as function of temperature. (Figure shown below)
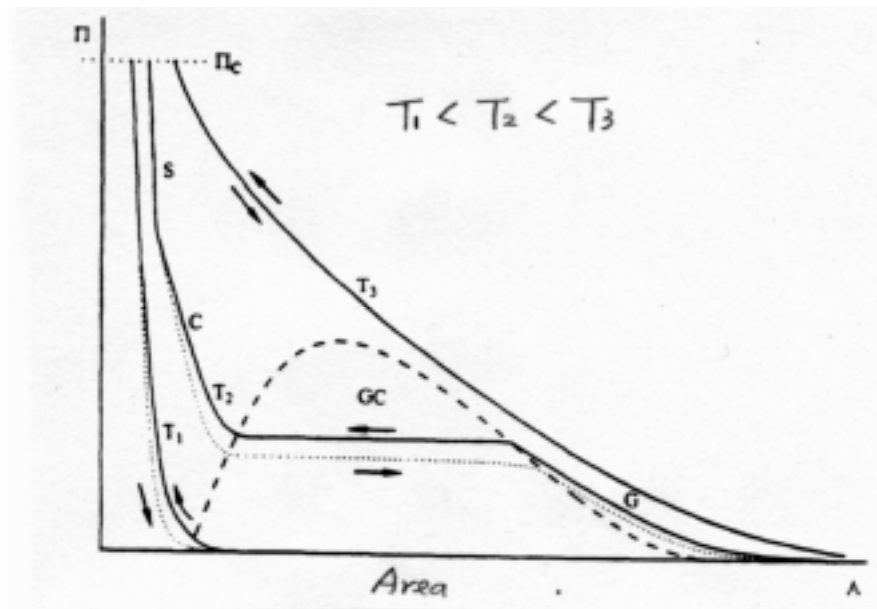

Fig. IV-15. States of monolayers (schematic).

Effects of Changes in the Nature of the Substrate (Subphase)

● Nature of subphase: pH, *concentration* and *valence* of solute ions.

● *For carboxylic acid:*

At low pH value → acid tends to be unionized → solid or condensed films

At high pH value → head group ionized is enhanced → repulsion force increased → expanded film

For amines: the effect is opposite to carboxylic acid.

● **In the presence of polyvalent ions (Ca^{2+} for example):**

Each cation associates with two acid molecules (form metal salt) results in a tighter packing and formation of solid or condensed film.

● For ionized species: subphase containing neutral electrolyte (NaCl) can reduce the electrostatic repulsion between the head groups and thereby enhance packing efficiency.

8.5.5 Mixed-Film Formation

Types of the mixed monolayers may vary between two extreme cases:

(1) *ideal solution*: the interaction between the two materials is the same as that between the pure materials. That is, no "*special interactions*" between various materials. ----ex. Two normal-chain carboxylic acid (**Fig. 8.19a**), the characteristics of the mixed monolayer lies between those of the pure materials.

■ If dissimilar materials are mixed that can undergo specific interactions (e.g., **alcohols** is added to **carboxylic acids**), the acid monolayer becomes more condensed----because alcohol can under go strong specific interaction with acid (hydrogen bounding) ------(**Fig. 8.19b**)

(2) *immiscible system*: two materials are sufficiently different and no specific interaction.

- ■ Increasing the surface pressure may cause the expulsion of one component from the surface (**Fig. 8.19c**).

- ■ two materials may form a heterogeneous film, with islands (2-dimensional micelles) of one film "floating" in a sea of the other (**Fig. 8.19 d**)
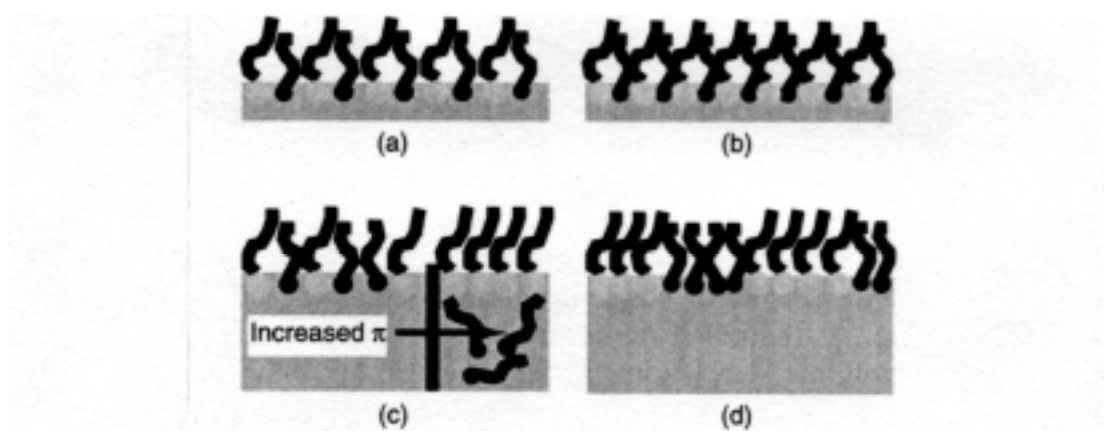

FIGURE 8.19. Mixed molecular films can have several possible structures. (*a*) An "idel" mixed film is one that has a homogeneous distribution of components throughout the film, but with no "special" interactions between components. (*b*) A synergistic mixed film or complex involves specific interactions between component molecules that produce characteristics different from those expected for an ideal film. (*c*) Immiscible components may produce the expulsion of the more soluble component of the mixture at high surface pressure. (*d*) Heterogeneous mixed films may form "islands" (two-dimensional micelles?) of the components.

- ● Important phenomenon of mixed film in biological and medical area:
  --- *mimic phenomena in biological system (cell walls and membrane)*

  - ■ Film penetration: soluble surface-active materials in the subphase enters into the surface film to alter its nature significantly, or to under go physical or chemical processes (**Fig. 8.20**)----cell surface reactions, catalysis, transport across membrane.

- Typical penetration experiment --- formation of an insoluble monolayer at a surface pressure π, after which a soluble surface-active material is injected below the monolayer and changes in surface pressure (at constant area) due to penetration or inclusion of the new material in the monolayer. Also changes in surface area, surface potential and *etc.* can be studied.
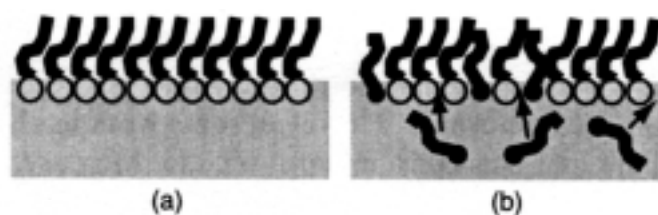

(a)   (b)

FIGURE 8.20. Film penetration is a potentially important process in which a monomolecular film (*a*) is modified by the insertion of molecules of a second component from the supporting solution (*b*). In the process, the second component penetrates the original monolayer film from solution to produce a mixed film with new properties.

8.5.6 Surface Films of Polymers and Proteins

- Because the length of the polymer molecules and the complex interactions involved in intra- and interchain interactions, the properties of such films are les distinct and more difficult to determine

  - It takes long time for a macro-molecular film to get its true equilibrium state.

  - When carried out carefully, a great deal of interesting information about the macromolecules can

### 8.5.7. Monolayer Films at Liquid-Liquid Interface and on Nonaqueous Liquids

● At a water-nonpolar liquid interface: the area per molecule of alcohols and carboxylic acids is larger than that spread at the water-air interface.

---- **Reason**: the presence of nonpolar liquid reduces the lateral cohesive interaction between adjacent tails (swelling of the monolayer).

● Studies of monolayers on liquid other than water have been limited by experimental difficulties and lack of obvious practical relevance.

■ Systems had been done involve: Hg, long-chain hydrocarbons, mineral oil, etc.

■ For mercury, with high surface tension, adsorbs almost anything → difficult to maintain a clean Hg surface.

8.5.8. Deposited Monolayer and Multilayer Films

Transfer the monolayer at the gas-liquid interface to a solid substrtae----commonly referred to as the "**Langmuir-Blodgett technique**" and the film transferred is called "**Langmuir-Blodgett Film**"

● The solid substrate: glass, metal, mica -- any material that has a relatively strong affinity for one part of the monolayer material

● Type of the LB films (Figure 8.21)

● Wettability of LB film of carboxylic acid.

(a)

(b)
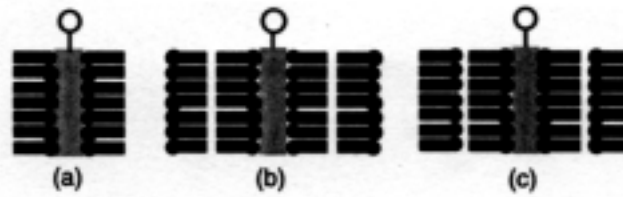
LB   a

  b
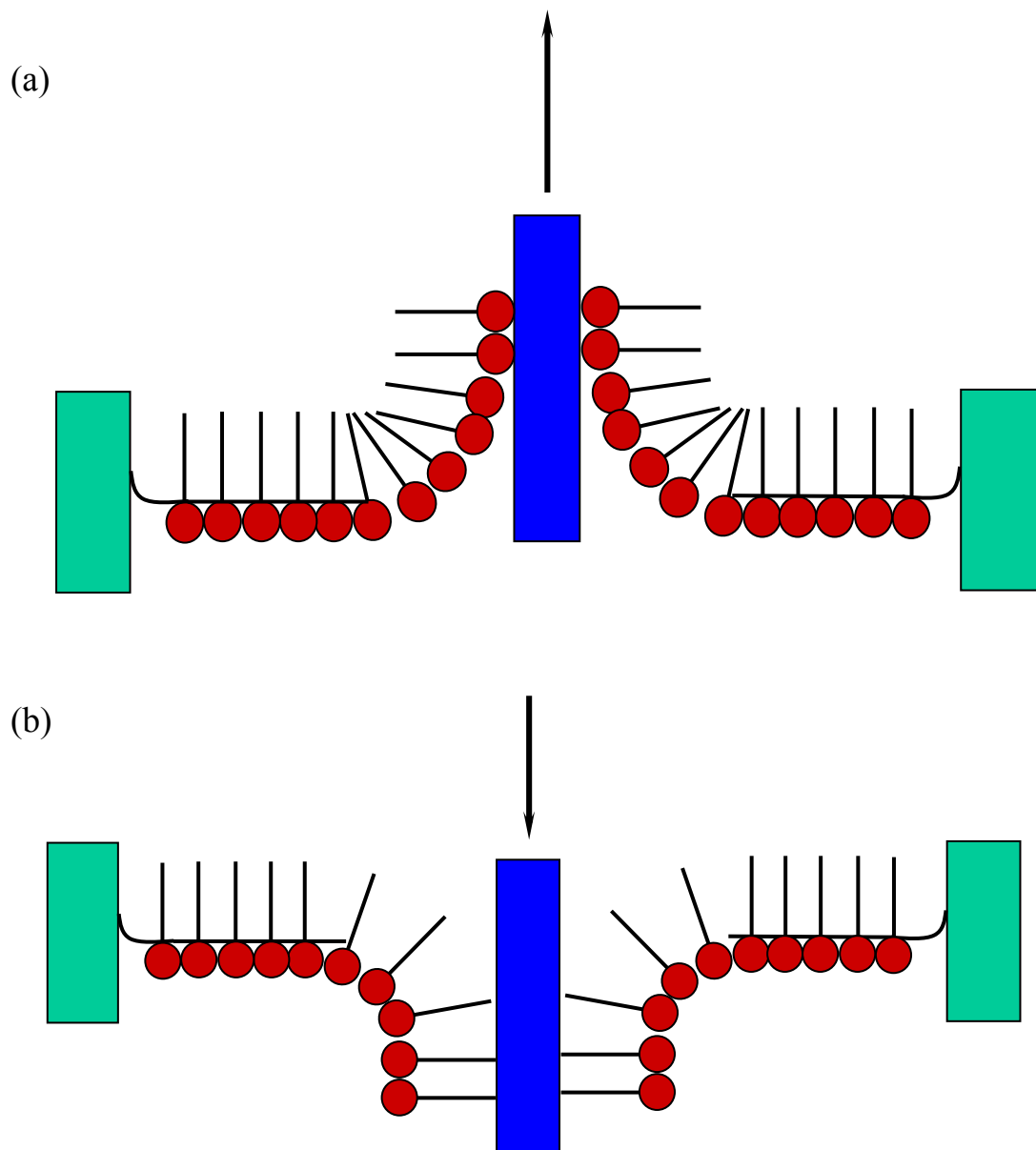
FIGURE 8.21. Insoluble monolayer films can, with careful work, be deposited onto solid substrates from the liquid surface. The so-called Langmuir–Blodgett films will usually have alternating molecular orientations: (a) first-layer deposition with the head (or tail) toward the solid substrate and (b) the second-layer head-to-head or tail-to-tail in a "Y" film orientation. Under some conditions it is possible to produce an "X" film with "head-to-tail" orientation (c).
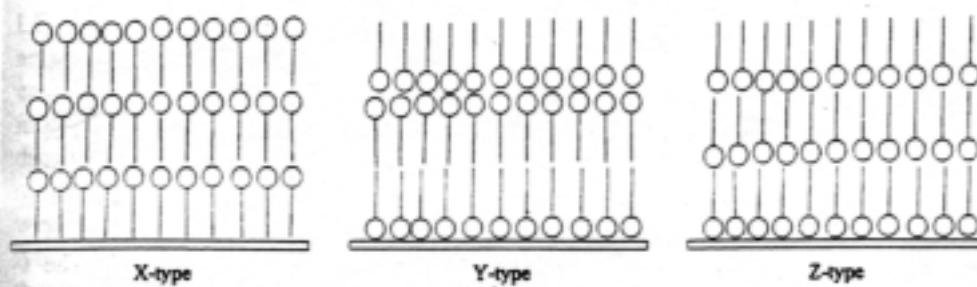

FIG. 2 Common modes of Langmuir–Blodgett film transfer: X-type, Y-type, and Z-type.
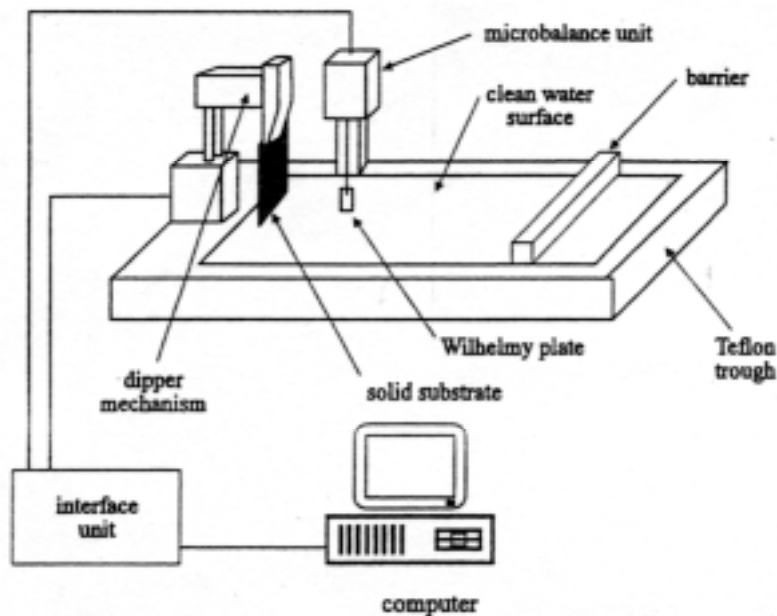

FIG. 1 Major components of a Langmuir–Blodgett trough.

LB   a   X-type

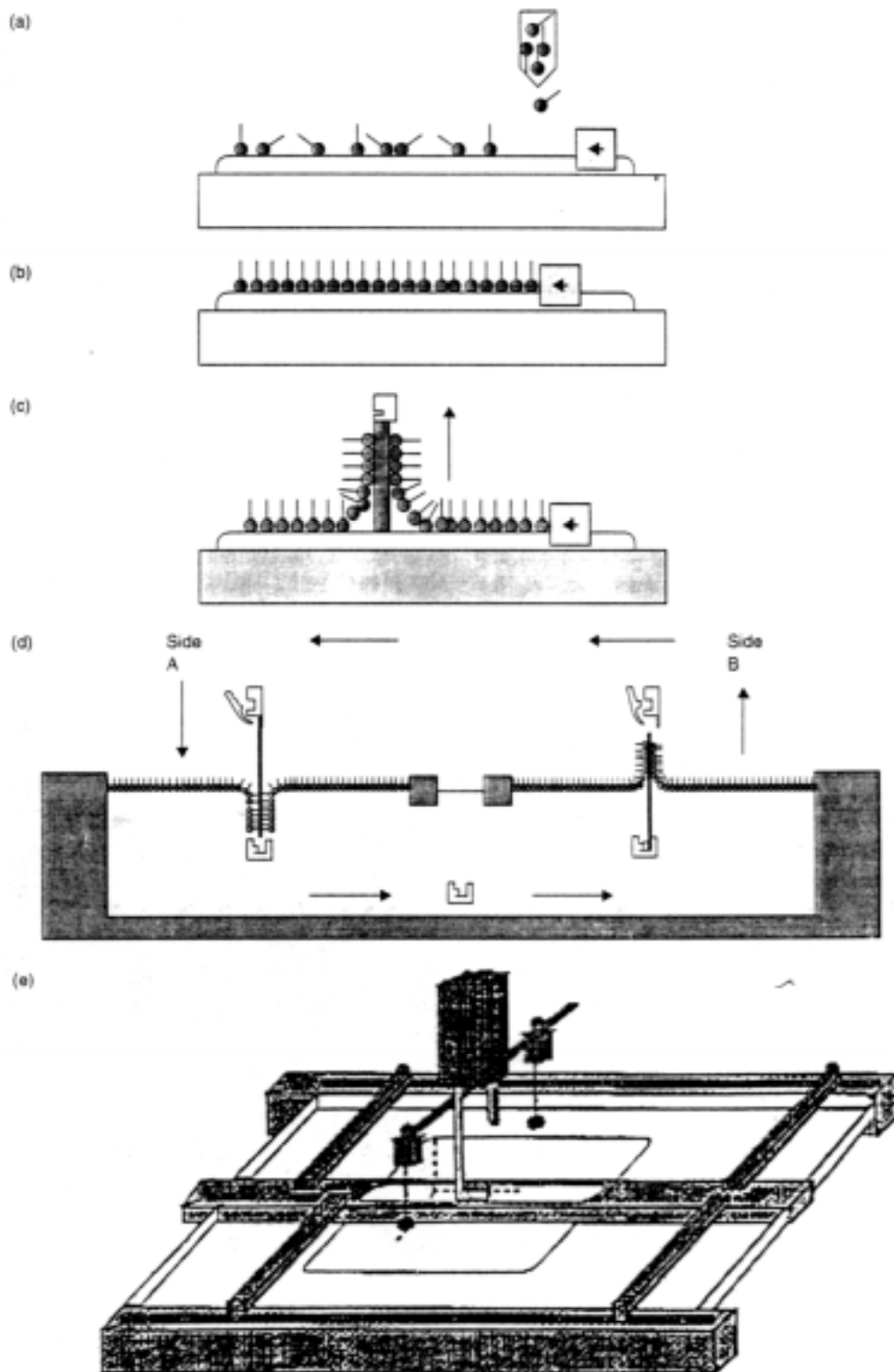   b   Z-type

       c   Y-type

Figure 5.1. Schematic of the Langmuir–Blogett deposition process. The amphiphile is dissolved in an organic solvent and subsequently spread at the air–water interface. The solvent evaporates and a monolayer of the amphiphile at the air–water interface remains (a). The monolayer at the air–water interface can be further manipulated by means of a movable barrier allowing control of the area per molecule (b). The Langmuir monolayer can be transferred by an up-stroke on to a hydrophilic surface (c) and via a down-stroke on to a hydrophobic surface. A dual compartment trough enables the simultaneous processing of two different materials (d), while a programmed dipping sequence allows the determination of layer architecture at a molecular level