Chapter 9 Adsorption

9.1 Introduction

Adsorption:

(i) the principle ways in which high-energy interfaces lower the overall energy of a system.

(ii) A complex process which is different to be described precisely by theoretical model.

■ **Definition of Adsorption :**

Preferential concentration of one component of a system at an interface, where the local concentration is different from those in the bulk phase.

(i) ”positive” adsorption: interfacial concentration of the adsorbed species is greater than that in the bulk phase. – decrease the interfacial energy.

(ii) ”negative” adsorption: increase the interfacial energy of a system.

■ **Two aspects that can be addressed in consideration of adsorption process:**

(i) Thermodynamics – concerns the final equilibrium interfacial energy.

(ii) Kinetics – the rate at which the adsorption process occurs.

9.1.1 The Gibbs Surface Excess

- **The interfacial region –** determined by the shape of concentration profile (Fig 9.1)

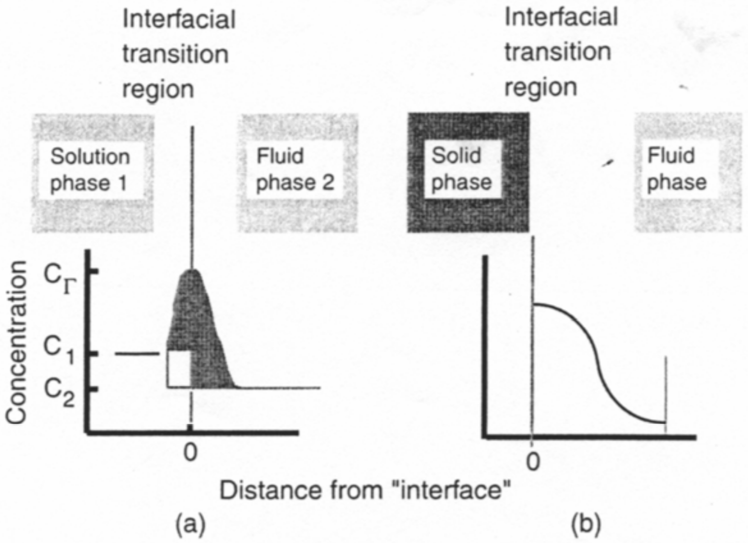

FIGURE 9.1. When a material is positively adsorbed at an interface, its adsorption profile will resemble (*a*) for a liquid–fluid interface or (*b*) for a solid–fluid interface.

- **Gibbs approach to determine the concentration of components in the interfacial region:**
  - Consider component i in two phase α, β

concentration: C_i^α, C_i^β
volume: V_α, V_β

Total amount i, (n_i), when the concentration is uniform through α, β phases

$$n_i = (C_i^\alpha V_\alpha + C_i^\beta V_\beta) \tag{9.1}$$

  - the local value of C_i varies going through the interface so the <u>surface excess amount of i</u> (n_i^σ) is given by

$$n_i^\sigma = n_i - (C_i^\alpha V_\alpha + C_i^\beta V_\beta) \tag{9.2}$$

n_i: the real amount of i

- The surface excess can also be considered to be the amount of i adsorbed at the interface.

  * Problem arises: how to define the interface between α and β.

  * **Gibbs' approach** (*Gibbs dividing surface*):
  the interface was defined as *a position that the surface excess of example substance (always the solvent) becomes zero*.– (Fig 9.2a, 2b)

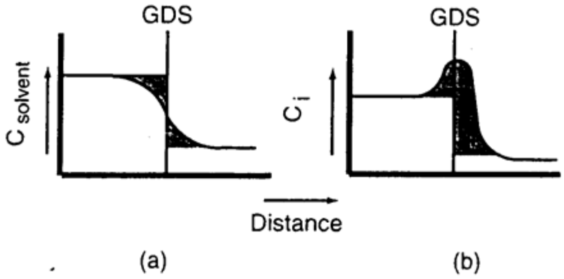

FIGURE 9.2. In the Gibbs approach to defining the surface excess concentration, the Gibbs dividing surface (GDS) is defined as the plane in which the solvent excess concentration becomes zero (the shaded area is equal on each side of the plane) as in (*a*). The surface excess of component *i* will then be the difference in the concentrations of that component on either side of that plane (the shaded area) (*b*).

- Surface excess concentration of i with respect to α substance, $\Gamma_i^{(\alpha)}$

$$\Gamma_i^{(\alpha)} = \frac{n_i^\sigma}{A^\sigma} \qquad A^\sigma\text{: interfacial area} \qquad (9.3)$$

- Surface excess quantity is difficult to measure directly. The measurements have been made at solid-liquid interfaces, but liq.-liq. and liq.-vapor interface still pose difficulties.

9.1.2 The Gibbs Adsorption Equation

The Helmholyt free energy (F) of bulk phase, α;

$$F^\alpha = -S^\alpha T^\alpha - P^\alpha V^\alpha + \Sigma\mu_i^\alpha n_i^\alpha \qquad (9.4)$$

In differential form (with constant P)

$$dF^\alpha = -S^\alpha dT^\alpha - P^\alpha dV^\alpha + \Sigma\mu_i^\alpha dn_i^\alpha \qquad (9.5)$$

The total energy for a two phase system (α, β, α - β)

$$F^T = F^\alpha + F^\beta + F^\sigma \tag{9.6}$$

F^σ: interfacial excess free energy (usually ignored when the interfacial area is small) for colloidal system (with large surface area), the free energy of the interface may be the primary factor.

- **The derivative of the surface free energy (analogous to 9.5)**

$$dF^\sigma = -S^\sigma dT + \sigma dA^\sigma + \Sigma \mu_i dn_i^\sigma \tag{9.7}$$

$- P^\alpha dV^\alpha$ in Eq.(9.5) is replaced by σdA^σ in eq.(9.7)

the opposite sign is because :
σ: a tension (pulling force)
P: a pressure (pushing)

- **At constant T, P, μ_i, at equilibrium**

for α phase:

$$dF^\alpha = V^\alpha dP^\alpha - S^\alpha dT + \Sigma n_i^\alpha d\mu_i^\alpha = 0 \tag{9.9}$$

for interfacial phase (σ) ----- Gibbs adsorption Eq.

$$-A^\sigma d\sigma - S^\sigma dT + \Sigma n_i^\sigma d\mu_i = 0 \tag{9.10}$$

At constant T

$$-d\sigma = \frac{\sum n_i^\sigma d\mu_i}{A^\sigma} \tag{9.11}$$

$$-d\sigma = \sum \Gamma_i d\mu_i \tag{9.12}$$

- For a two-component, liquid-vapor system, the surface excess concentration of solvent is zero ($\Gamma^\alpha = 0$), Eq.(9.12) becomes: (general form of Gibbs adsorption Eq.)

$$d\sigma = -\Gamma_2^{(1)} d\mu_2 \tag{9.13}$$

"2" designates a solute dissolved in bulk phase 1.

- At equilibrium

  μ_i (interface) = μ_i (phase α, β in bulk phase)

$$d\mu_2 = RTd \ln a_2^{(1)} = RTd \ln x_2\gamma_2 \qquad (9.14)$$

$a_2^{(1)}$: activity of 2 in (1) of the bulk phase
x_2: mole fraction
γ_2: activity coefficient

Eq.(9.13) ⇒ $d\sigma = -RT\Gamma_2^{(1)} d \ln x_2\gamma_2$ (9.15)

For positive adsorption:
x_2 (or μ_2) increase → increase $\Gamma_2^{(1)}$
→ decrease in interfacial tension , σ

- **For a surface active material (surfactant), $x_2\gamma_2 = c_2$**

$$\Gamma_2^{(1)} = -\frac{1}{RT}\left[\frac{d\sigma}{d \ln c_2}\right] \qquad (9.16)$$

- Practical application of Eq.(9.16) :
  Determine the surface activity, surface concentration, from the measurement of σ as a function of c_2.
- The importance of the adsorption control in various applications
  ⇒ described in text book. (p.185~186)

9.2 Adsorption at the solid-vapor interface

- Solid characteristics are history-dependent. So, detailed discussion of adsorption onto solid surfaces must include knowledge of "historical" elements.

- Method for a material to reduce surface energy
  Liquid: reducing the interfacial area (from spherical drop)
  Solid: adsorbing materials – heterogeneous in the distribution of excess surface energy, so, the adsorption is not a uniform process.

9.2.1 Energetic Considerations: physical adsorption versus Chemisorption

- **The forces involved in adsorption processes :**
  (a). Non-specific forces (physical adsorption) –
  Van der Walls forces, electrostatic forces
  (b). Specific forces (chemisorption) – –
  Chemical bounds

- **Vapor adsorbs on a solid surface is a spontaneous process –**
  overall free energy change(△G) : negative
  degree of freedom (△S) : decrease, negative

$$\Delta G = \Delta H - T\Delta S$$

For△ G to be negative, △H should be negative, that is, adsorption must be an exothermic process.

- The situation may be different in the solid/liquid system.

- **Measurement of heat of adsorption, △H –**
  by Clausius-Clapeyron equation

$$(\frac{\partial \ln p}{\partial T})_v = -\frac{\Delta H_{ads}}{RT^2}$$

for physical adsorption, $\triangle H_{ads} \approx$ heat of condensation

- For example : heat of condensation of N_2 = -6 KJ/mole

$\triangle H_{ads}$ of N_2 on iron = -10 KJ/ mole
on graphite = -12KJ/mole
on TiO_2 = -14 KJ/mole
chemisorption of N_2 on iron = -150 KJ/mole

- Physical adsorption is generally a *multilayer process*, not limited by the available solid surface area, *reversible*, *more rapid*, *occurs on almost all solid surface.*

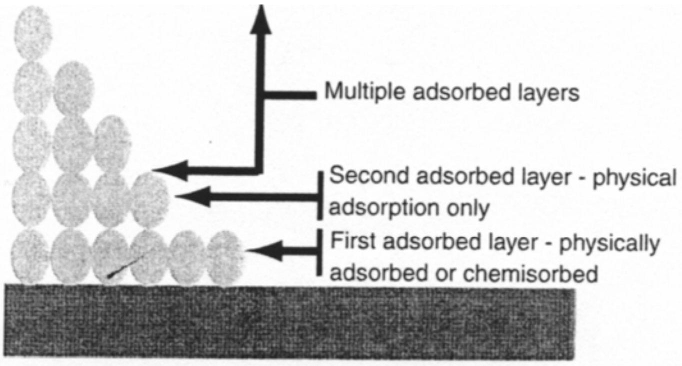

FIGURE 9.3. In multilayer adsorption on a solid surface the first adsorbed layer may be physically adsorbed or chemisorbed. Subsequent layers will be physically adsorbed.

- ***Chemisorption***: limited to the formation of a monomolecular adsorbed layer, has some activation energy, much slower than physical adsorption, may not be reversible.
- The energetic relationship between the physical and chemical adsorption

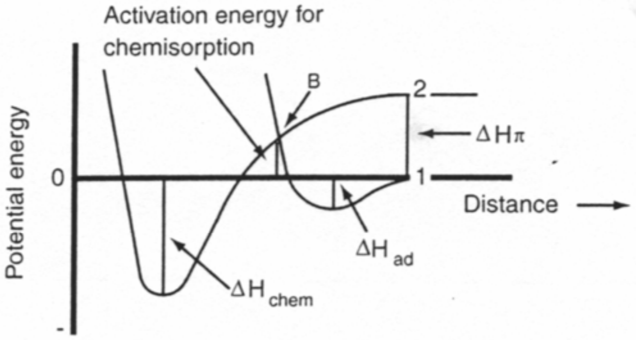

FIGURE 9.4. Although physical adsorption and chemisorption may be energetically quite different, the stronger chemisorption phenomenon must be preceeded by a physical adsorption process.

curve 1: physical adsorption

at large distance → no attraction between surface and vapor molecule

at short distance → attraction due to Van der Waals interaction

As distance decreases to that the electron clouds overlap → repulsive interaction

curve 2: chemisorption

involves change in molecular structure for a diatomic molecule (A_2), it may involve the rupture of π bond – the starting point is the energy of the bond being broken, $\triangle H_{\pi}$, which represent the activation energy of the process.

- If the two adsorption processes occur in a cooperative way, physical adsorption is an important component of the overall chemisorption process –
    - The point where curves 1 and 2 intersect becomes the activation energy for chemisorption.

- The adsorption of organic compounds on solid surface has critical effect on the application of that surface. (wetting, spreading…)

FIGURE 9.5. Even a monolayer of physically adsorbed material can have a disastrous effect on some technological processes, especially critical coating processes in which absolutely smooth, uniform coating is required such as the microelectronics industry. (*a*) An uncontaminated surface should produce a smooth, uniform coated layer. (*b*) Surface contamination by a lower-energy material (such as oil molecules) may result in the formation of "repellency" spots or other defects, producing less than optimum or even useless finished products.

9.2.2 Chemisorption and Heterogeneous Catalysis

- **The presence of a solid surface (forceful presence), can alter the chemical properties of an adsorbed molecular including:**

Electronic structure: electronic and vibrational spectra, chemical reactivity

⇒ leads to chemical reaction between two chemisorbed species.

- **Chemical reactions that involve the chemisorption :**

(1) Combination (hydrogen + alkene → alkane)
(2) Decomposition (ethanol → ethylene + H_2O)
(3) Polymerization (ethylene → polythylene)

⋮

- **The processes involved in the reaction mechanism of heterogeneous catalytic reactions:**
    (1) initial physical adsorption,
    (2) possible surface diffusion of the adsorbed species,
    (3) chemisorption processes (e.g., bond breaking)
    (4) chemical reaction between adsorbed species,
    (5) desorption of the product.

- All or only some of these steps may be involved.

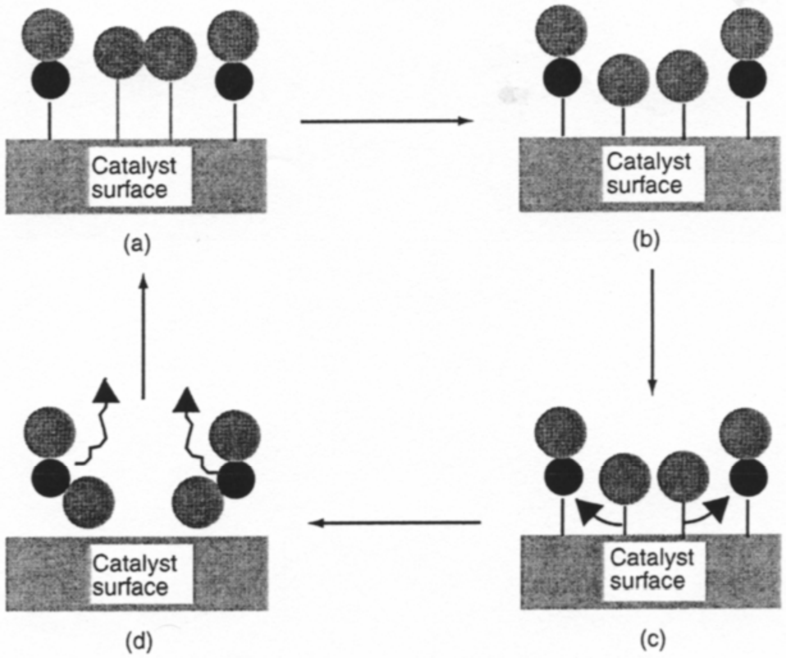

FIGURE 9.6. The heterogeneous catalysis process involves several adsorption and desorption steps before and after chemical reaction. The process for the catalytic conversion of carbon monoxide to carbon dioxide is the following (approximately): (*a*) carbon monoxide is adsorbed strongly through the carbon atom—molecular oxygen is adsorbed more weakly at both atoms; (*b*) the oxygen molecule is activated by splitting into two oxygen atoms; (*c*) the oxygen atoms react with neighboring adsorbed CO molecules to produce CO_2, which is only weakly adsorbed; (*d*) the CO_2 desorbs, diffuses away, and liberates the catalyst site for further reaction.

- An example for a hypothetical heterogeneous oxidation of A with O_2:

$$O_2 + 2A + catalyst \to 2AO + catalyst$$

Involves flowing steps:

A + catalyst → A (adsorbed) (K_1)

O_2 + catalyst → O_2 (adsorbed) (K_2)

O_2 (adsorbed) → O_2 (chemisorbed) → 2O • (K_3)

Surface diffusion of A, O (K_4)

A + O → AO (adsorbed) (K_5)

AO (adsorbed) → AO (desorbed) (K_6)

⇒ The subject of heterogeneous catalysis is very complex.

9.2.3 Catalytic Promoters and Poisons

Promoters: An additive that improves a catalytic reaction
Poison: An additive that ruins a catalytic reaction

■ **Promoters –**

- The exact role of promoters is not well understood, and is now related to the formation of specific electronic surface states necessary for reaction.
- *Example* : improvement the reaction activity of Haber ammonia synthesis ($N_2 + 3H_2 \to 2NH_3$, catalyst Fe_3O_4) by adding Al_2O_3, K_2O

■ **Poisons –**

- Such materials generally function by binding strongly and irreversibly to the surface sites.
- *Example*: Sulfur-containing compounds (especially thiols) adsorb strongly on metal. (The poison of catalytic converters in automobile exhaust.)

9.3 Solid-Vapor Adsorption Isotherms

Adsorption isotherm: the amount of gas (volume, V) adsorbed as a function of gas pressure (P) at a constant temperature

Isobar: *V* v.s. *T* at constant P

Isosteres: *P* v.s. *T* at constant V (used to determine ΔH_{ad} using the Clausius-Clapeyron Eq.)

9.3.1. Classification of Adsorption Isotherm

The phenomena involved in the process that should be considered in an adsorption model:

(a). Initial monomolecular adsorption : at low and high coverage,
(b). Multilayer adsorption,
(c). Chemisorption,
(d). Capillary condensation.

Five major isotherm types are generally considered.

- **Type I isotherm – Langmuir type**
  - Rapid rise in the initial adsorption stage with increasing gas pressure, and attain a complete monolayer coverage
  - Occurs in chemisorption (limited to a monolayer), for system with strong attractive interaction between adsorbate and adsorbent, but weak interaction between the adsorbate themselves; for solid with fine microporous structure

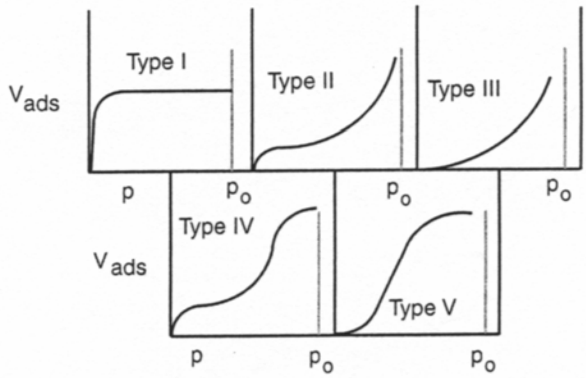

FIGURE 9.7. Adsorption isotherms are generally divided into five main types depending on the degree of adsorption (monolayer or multilayer), the mechanism of adsorption (physical or chemisorption), the nature of the adsorbent surface (porous or nonporous), and the relative strengths of adsorbate–adsorbent interactions.

- **Type II isotherm – typical physical adsorption on nonporous solid.**
  - The adsorbate molecules have strong mutual interactions, which leads to a multilayer adsorption.
  - Complete monolayer coverage attains first (at point B) and then multilayer formation begins.
- **Types III and V**
  - For systems in which the interaction between adsorbate molecules is stronger than that between adsorbate and adsorbent.
  - The uptake of gas molecules is initially slow, and until surface coverage is sufficient so that the interactions between adsorbed and free molecules begins to dominate the process. (autocatalytic process)
- **Type IV**
  - Similar to type II, usually correspond to system involving capillary condensation in porous solids.
  - Once the pores are filled, further adsorption to form multilayer does not occur and a plateau region results. (a weak interaction between the adsorbate molecules)

9.3.2 The Langmuir Isotherm

Assumptions:

(1) Monolayer adsorption
(2) Localized adsorption (occur on specific sites)
(3) Heat of adsorption is constant. (independent of the amount of material adsorbed)
(4) Based on kinetic model of adsorption-desorption process

Rate of adsorption: $k_A P (N - n)$
Rate of desorption: $k_D n$

where k_A, k_D : rate constant,
P: pressure of the adsorbate
N: total number of adsorption sites
n: number of occupied sites.

At equilibrium:

$$k_A P (N - n) = k_D n \tag{9.19}$$

the equilibrium constant, $K_{eq} = k_A/k_D$

$$K_{eq} = \frac{n}{p(N-n)} = \exp\frac{-\Delta H^0}{RT} \tag{9.20}$$

$\triangle H°$: heat of adsorption at temperature T and standard pressure, P_{ST}

The fraction of the adsorption sites occupied, q, is

$$q = \frac{n}{N} \tag{9.21}$$

Eq. (9.20) can be written as

$$q = \frac{K_{eq}P}{1 + K_{eq}P} \tag{9.22}$$

or

$$q = \frac{P}{P + K_{eq}^{-1}} = \frac{P}{P + P_{st}\exp(\Delta H^0 / R)} \qquad (9.23)$$

Eq. (9.22) can be rearranged to a linearized form

$$n^{-1} = N^{-1} + (K_{eq}NP)^{-1} \qquad (9.24)$$

or, $p/V = p/V_m + 1/(aV_m)$

- A plot of n^{-1} v.s. P^{-1} should be linear -

  Slop → K_{eq}; intercept→ N

- If the plot is not linear, then the Langmuir model can not fit the adsorption process.

9.3.3 The Freundlich Adsorption Isotherm

$$V = KP^{1/a} \qquad (9.25)$$

V: volume of adsorbed gas

K, a : constant (a is usually >1)

- Freundlich can be derived theoretically with the assumption that ΔH_{ad} varies exponentially with the extent of surface coverage.

  (closer to reality than the Langmuir assumption)

By taking the logarithm of Eg.(9.25)

$$\ln V = \ln K + (1/a)\ln p \qquad (9.26)$$

- A plot of (ln V) v.s. (ln p) gives a straight line

9.3.4 The Brunauer-Emmett-Teller (BET) Isotherm

Assumptions:

(1) multilayer adsorption;

(2) adsorption of first layer has a heat of adsorption, ΔH_A;

(3) the subsequent layers are controlled by heat of condensation, ΔH_L.

- **The linearized form of BET equation**

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0} \tag{9.27}$$

V: volume of adsorbed vapor at STP

V_m: monolayer capacity at STP

P: partial pressure of the adsorbate

P_o: saturation vapor pressure of the adsorbate

$C \approx \exp[(\Delta H_A - \Delta H_L)/RT]$ (9.28)

- BET Eg. was developed primarily to describe the type II isotherm (N_2, Ar…on polar surface, $C \approx 100$)
- It reduces to the Langmuir isotherm at low pressure and monolayer coverage($\Delta H_A >> \Delta H_L$)

⇨ at such situation $P_o >> P$, $C \sim (C-1)$

Eg. (9.27) becomes

$$\frac{P}{VP_0} = \frac{1}{V_m C} + \frac{P}{V_m P_0}$$ ………. Langmuir isotherm

- when first adsorption is less exothermic ($\Delta H_A < \Delta H_L$), $C<1$, describes type III isotherm

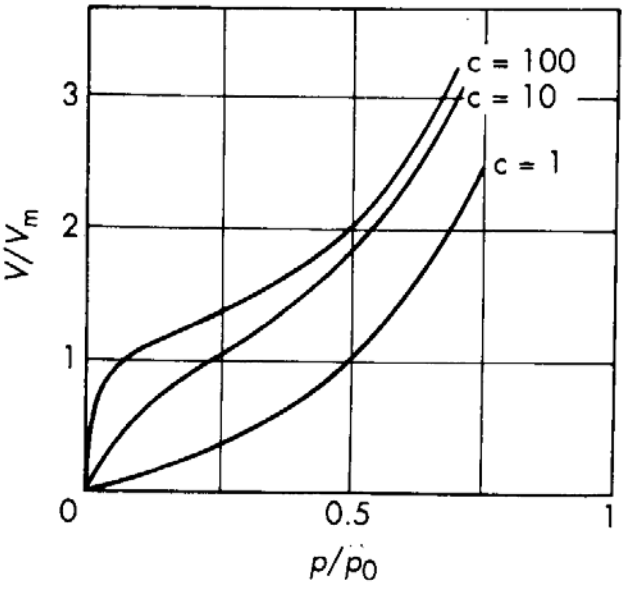

Figure 5.11 BET isotherms

9.3.5 Surface Areas from the BET Isotherm

V_m → surface area (As)

From Eq. (9.27), $\frac{P}{V(P_0-P)}=\frac{1}{V_m C}+\frac{(C-1)P}{V_m C P_0}$, a plot of

$$\frac{P}{[V(P_0)-P]} \quad \text{v.s.} \quad \frac{P}{P_0} \rightarrow \textit{linear}$$

Slope, $S=\frac{(c-1)}{V_m C}$

Intercept, $I=\frac{1}{V_m C}$

Then

$$V_m=\frac{1}{S+I} \tag{9.29}$$

$$A_s=\frac{V_m K}{sample\ weight} \tag{9.30}$$

$$K=\frac{N_A A}{M_V} \tag{9.31}$$

A: area per molecule
M_v: volume per mole of gas

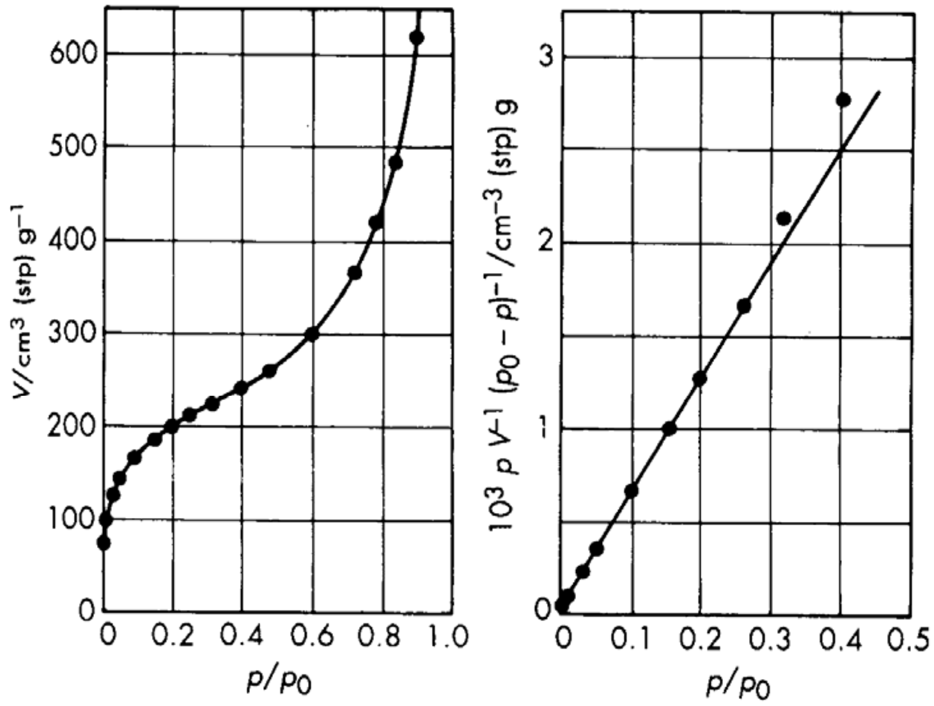

Figure 5.13 Isotherm and BET plot for the multilayer adsorption of nitrogen on a non-porous sample of silica gel at 77 K

- N_2 is the most commonly gas employed for BET surface area determination (A=0.162nm^2 at 77K)
  - N_2 gives a well-defined value of B point in Fig. 9.7 (ie.-$\triangle H_A$>> -$\triangle H_L$) , and -$\triangle H_A$ is not too high to prevent excessive localization
  - Other gases used : Ar (A=0.138nm^2)
    Krypton (A=0.195nm^2)

9.4 Adsorption at Solid-Liquid Interfaces

The importance of solid-liquid adsorption involves in:

biological system (joint lubrication , implant rejection …)

mechanics (adhesion , lubrication)

agriculture (soil wetting…)

electronic (microcircuit fabrication)

energy production(secondary and tertiary oil recovery)

paint production(pigment dispersion, stabilization)

9.5 The Adsorption Model

A transition region formed between bulk solid and the bulk liquid for both solvent (Fig 9.8a) and solute (Fig 9.8b)

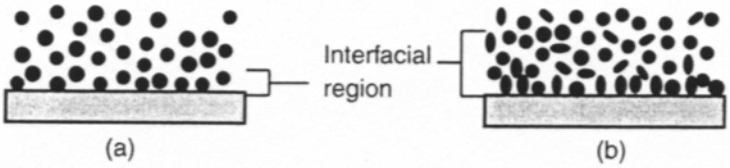

FIGURE 9.8. At a solid–liquid interface two adsorption "situations" may be encountered: (*a*) in the case of a pure liquid, the molecular distribution will be approximately uniform, although some molecules may be adsorbed to produce a small surface excess (black circles); (*b*) for a solution of surface-active solute (black ovals), extensive adsorption will occur, producing a significant interfacial region of excess solute concentration.

- A higher concentration of solute near the interface →positive adsorption (Fig 9.8b)

- Adsorption at solid-liquild interface may be small and can be negligible.

- The adsorption may even be negative ---for system one or more components are strongly adsorbed at the interface and lower the interfacial tension.

- Quantitative and qualitative points that are of interest for adsorption from liquid onto solid:
  1. amount of material adsorbed per unit mass or area
  2. the solute concentration require to produce a given surface coverage (including saturation)
  3. the orientation of the adsorbed molecules on the surface.
  4. the effect of adsorption on the properties of the solid.

⇒ conventional method : by way of adsorption isotherm.

9.6 Quantification of Solid Adsorption

Quantitative equation describing the adsorption of one component in a binary solution. When the solution is dilute and the solute (2) is much more strongly adsorbed than the solvent (1)

$$n_2\sigma = \frac{\Delta n_2}{m} = \frac{\Delta C_2 V}{m} \qquad ? \qquad (9.34)$$

n_2: molar number of solute adsorbed at equilibrium
m: mass of solid adsorbent
V: volume of liquid phase in liters
ΔC_2: = C_{20} - C_2 (molar concentration of solute before adsorption, C_{20}, and at equilibrium, C_2)

- that is, the amount of adsorption (Δn_2) can be calculated from the concentration difference of the bulk liquid (ΔC_2)

9.6.1 Adsorption Isotherms in Solid-Liquid Systems

- Adsorption isotherm ➔ for evaluation the adsorption mechanism
- Interaction between adsorbent and adsorbate may fall into two categories : (1) weak and reversible physical adsorption, (2) stronger, irreversible or chemisorption
- The isotherm can be classified into four fundamental isotherm shapes based on the form at low concentrations (Fig.9.9)

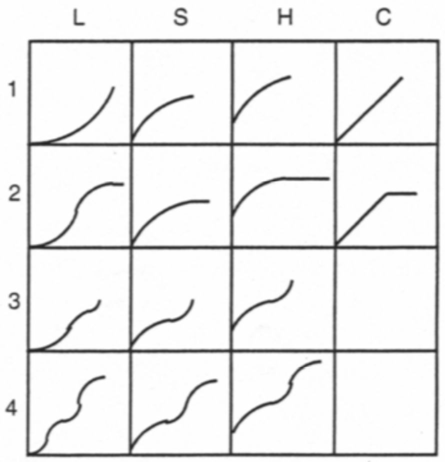

FIGURE 9.9. Various isotherm shapes are encountered in adsorption from solution. The more common shapes are illustrated here.

- L-class (Lamgmutir) isotherm: is identified by having its initial region concave to the concentration axis. As concentration of adsorbate increases, it reaches a plateau (L_2)and then L_3,L_4.(type I, II, IV in Fig9.7)

- S-class: initial slope is convex to the concentration axis (S_1),and then S_2 →S_4.(type III,V in Fig9.7)

- H-class (high affinity): a very strong adsorption at low adsorbate concentrations. The isotherm has a positive intercept on the ordinate.

- C-class: exhibits an initial linear portion of isotherm, indicating a constant partitioning of the adsorbate between the solution and the solid----occur in solid with microporous structure, but not for homogeneous solid surfaces.

9.6.2 Adsorption and Modification of Solid-Liquid Interface

The importance and applications of surfactant adsorption onto a solid surface from solution:

(a). remove unwanted materials from a system (detergency)
(b). change the wetting characteristics (coating, waterproofing)
(c). dispersion stabilization

- In these applications, the ability of surfactant to adsorb at the solid-liquid interface with a specific orientation and produce a desired effect is controlled by the chemical natures of the components: ***the solid, the surfactant, and the solvent.***

9.6.3 Adsorption and Nature of the Adsorbent Surface

- The nature of the solid surface is a major factor in determining the mode and extent of solution adsorption.

- Three principal groups of adsorbent surface:
  (1) non-polar and hydrophobic surface –polyethylene;
  (2) polar but do not process significant surface charges; (polyesters, natural fiber such as cotton)
  (3) possess strongly charged surface sites

(1) Nonpolar, Hydrophobic Surfaces:

- occurs as a result of dispersion force interactions

- orientation of surfactant in aqueous solution:
  hydrophobic tail associates with solid surface,
  hydrophilic head directs toward the the aqueous phase

- surfactant orientation changes with increasing degree of adsorption (Fig. 9.10)

"trains" → L shape → perpendicular

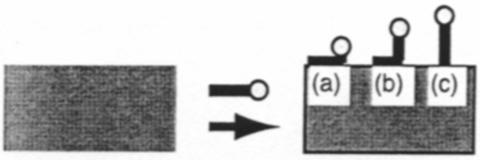

FIGURE 9.10. When a surfactant adsorbs on a solid surface, it may assume one (or more) of several orientations, depending on the natures of the surface and the molecule. For nonpolar surfaces the options will include (*a*) "trains" lying more or less flat on the surface; (*b*) "L"s, in which significant portions of the molecule remain adsorbed parallel to the surface; and (*c*) vertical or perpendicular in which the major portion of the chain has no direct contact with the solid surface.

- The surface saturation is attained near the CMC of the surfactant

- Since the hydrophilic group directed outward, there will normally be no inclination for the formation of a second adsorbed layer. (limited to monolayer)

- In non-aqueous solvent- less studies were made.
  example: dispersion of carbon black and crosslinked polymer in non-polar solvent.
  orientation of the adsorbed molecules: more or less parallel to the surface.

(2) Polar, Uncharged Surfaces:

- Include polyesters, polyamides, polyacrylates, cotton, silk.

- The adsorption mechanism is important in terms of dyeing processes, waterproofing, and detergency.

- The molecular orientation will be determined by a balance of several forces. → much more complex mechanism.

- The forces involved for a polar surface:
  dispersion force, dipolar interaction, hydrogen bonding, acid – base interactions ---- the relative balance between them determines the mode of adsorption.
  - dispersion forces predominate → equivalent to that of the nonpolar surfaces (Fig.9.10)
  - polar interaction dominate → hydrophilic head faces to the solid surface (Fig. 9.11)

- Effects of solvent:
  The relative strength of solvent- adsorbent, and solvent - adsorbate interaction also affects the final orientation.
  - A small change in the solvent (pH, electrolyte content, presence of a cosolvent) may reverse the adsorption type.

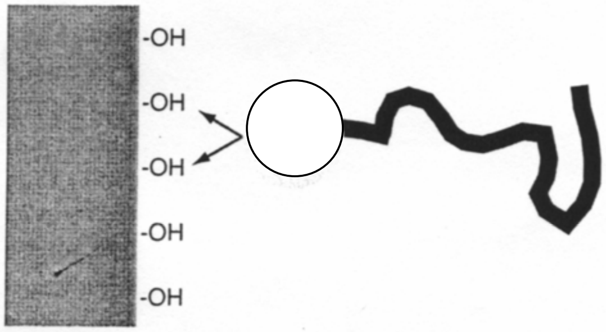

FIGURE 9.11. In adsorption in which the solid surface has a significantly polar character, the surfactant may orient itself with the polar head group toward the surface and the tail toward the solution.

(3) Surfaces Having Discrete Electrical Charges:

- A more complex process – capable of undergoing adsorption by the previously mentioned mechanisms.

- More sensitive to external conditions: pH, electrolyte, the presence of nonsurface-active cosolutes.

- Materials processing charge:

  oxides (silica, alumina, titania, etc.),
  salts (silver halides),
  latex polymers containing ionic comonomers,
  natural surface (protein, cellulosics)

- The dominant mechanism for such adsorption process go from:

  ion exchange → ion bounding (ion pair) → dispersion (hydrophobic interaction) ---- (Fig. 9.12)

- The three mechanisms involved in the adsorption: (Fig. 9.12)
  - region 1: ion exchange
    → The adsorbed counterions are displaced by surfactant molecules.
    → The electrical characteristics (charge and potential) unchanged.
  - region 2 : ion pairing
    → Resulting in a net decrease in surface charge.
    → The rate of adsorption will increase significantly due to the lateral interaction between hydrophobic groups of adsorbed surfactants (formation of aggregate structure or hemimicelles).

- region 3 : complete neutralization of the native surface charge (zero point charge)
  → The onset of dispersion force−dominated adsorption.

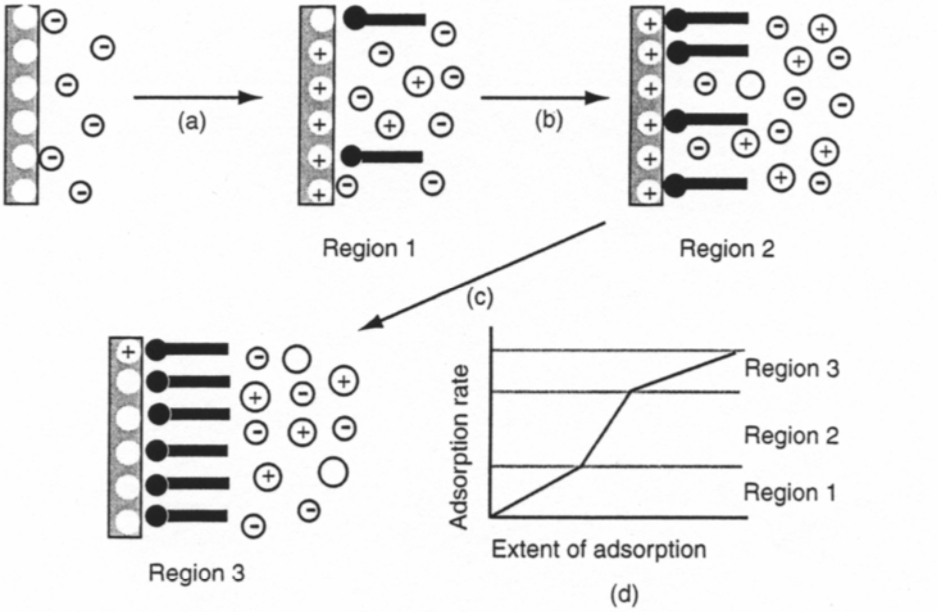

FIGURE 9.12. In the adsorption of an ionic surfactant onto a surface of opposite charge several stages will be encountered: (*a*) ion exchange, in which the native surface counterion will be exchanged 1 : 1 for surfactant molecules; (*b*) ion pairing, in which excess surfactant molecules are adsorbed (over the number of native ions bound to the surface); (*c*) charge neutralization, in which all accessible surface charges are neutralized by surfactant ions. Each stage of the process will have a characteristic adsorption profile as illustrated schematically (*d*).

9.6.4 Environmental Effects on Adsorption

- Important environmental conditions:
  Electrolyte content, pH,

- In high electrolyte concentrations (high degree of bound counterions): ion exchange is the only mechanism of adsorption other than dispersion.
  → The adsorption isotherm is almost linear.

- An increase in electrolyte content
  - → cause a decrease in adsorption of opposite charge
  - → increase of adsorption of like charged molecules (Fig. 9.13)

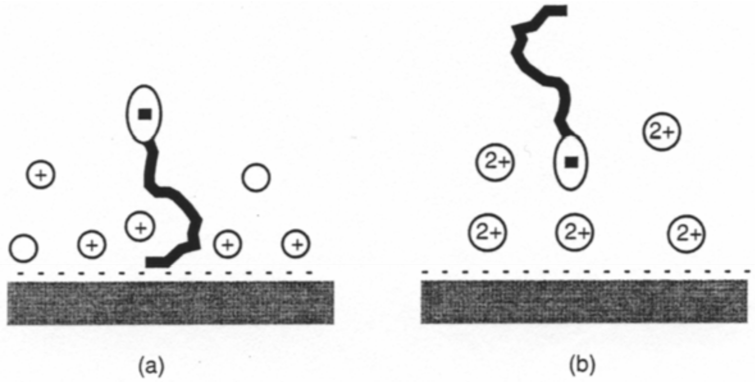

FIGURE 9.13. In systems of negatively charged surfaces and anionic surfactants, the presence of polyvalent cations such as Ca^{+2} and Al^{+3}, can produce "bridging" phenomena that result in strong surface–surfactant interactions that would not occur in the presence of monovalent ions such as Na^+ or K^+.

  - → important exception:

    the added cation has a specific interaction with the surfactant that reduces its solubility in the solution leading to enhanced adsorption.

    example: adding of polyvalent cations to carboxylic acid soaps.

- The presence of polyvalent cations (Ca^{2+}, Al^{3+}…) generally increases the adsorption of anionic surfactants onto negatively charged surface (Fig. 9.13b)
  - → ions are tightly bound to surface, neutralizing charge repulsions, and serve as bridging ion by association with both the negative surface and anionic surfactant head group.

- On solid surface having weak acid or base groups (protein, cellulosics, polyacrylates): sensitive to pH.
  - → pH is reduced → surface tends to more positive (positive charge or suppress the ionization of acid)
  - ● more favorable for the adsorption of anionic surfactant. (for both carboxylic acid and amine surfaces)

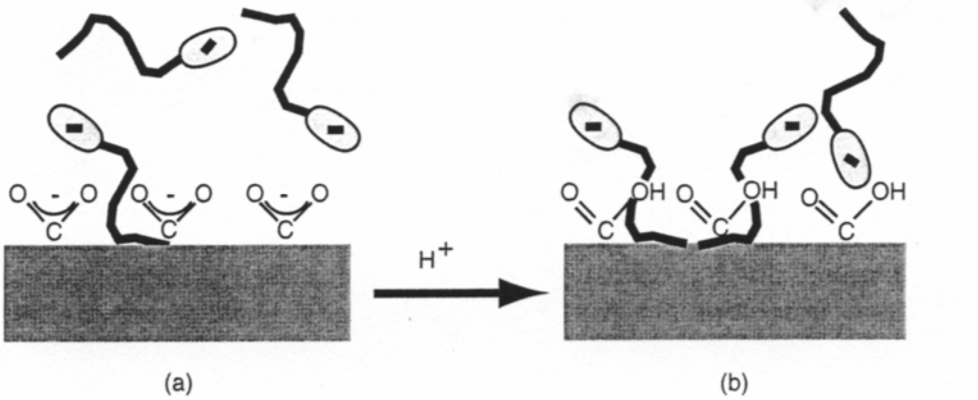

FIGURE 9.14. When the charge on a surface resulting from the ionization of a weak acid or base is neutralized, the propensity of a surfactant of like charge to adsorb on the surface is increased: (*a*) with charge, a surfactant of like charge can adsorb only by dispersion interaction, if at all; (*b*) with a neutralized charge, adsorption becomes more favorable, even to the extent of adsorbing through head group interactions.

- Temperature effects:

  As temperature increase,

  → decrease in the adsorption of ionic surfactants.(increase the solubility in bulk aqueous solution)

  → adsorption will increase for nonionic surfactant. (decrease in solubility)

9.6.5 Effects of Adsorption on the Nature of the Solid Surface

The resultant effect of surfactant adsorption on the surface character depends on the dominant mechanism of adsorption.

- For a highly charged surface:
  - If ion exchange is dominant → electrical natural will not be altered significantly
  - If ion pairing is important → the zeta potential will decrease or even be neutralized. (the solubility of a dispersed system become worse) (Fig. 9.15a)

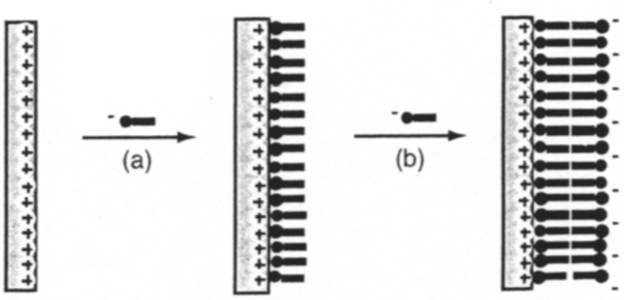

FIGURE 9.15. The interaction of an ionic surfactant with a surface of opposite charge will lead to charge neutralization (*a*) followed, in many cases, by charge reversal (*b*). Counterions are omitted for clarity.

- When the surface is neutralized by ion pairing of surfactant, the surfaces are hydrophobic, and it is possible for adsorption to continue by dispersion force interaction and leads to reverse of charge and instability. (Fig. 9.15b)

- For a water wetted surface, the adsorption of surfactant reduces the wettability, and its interaction with non-polar phase (oil, air) is more favorable.

  Application example: froth flotation of mineral ore.