Chapter 6

SURFACE CHEMISTRY

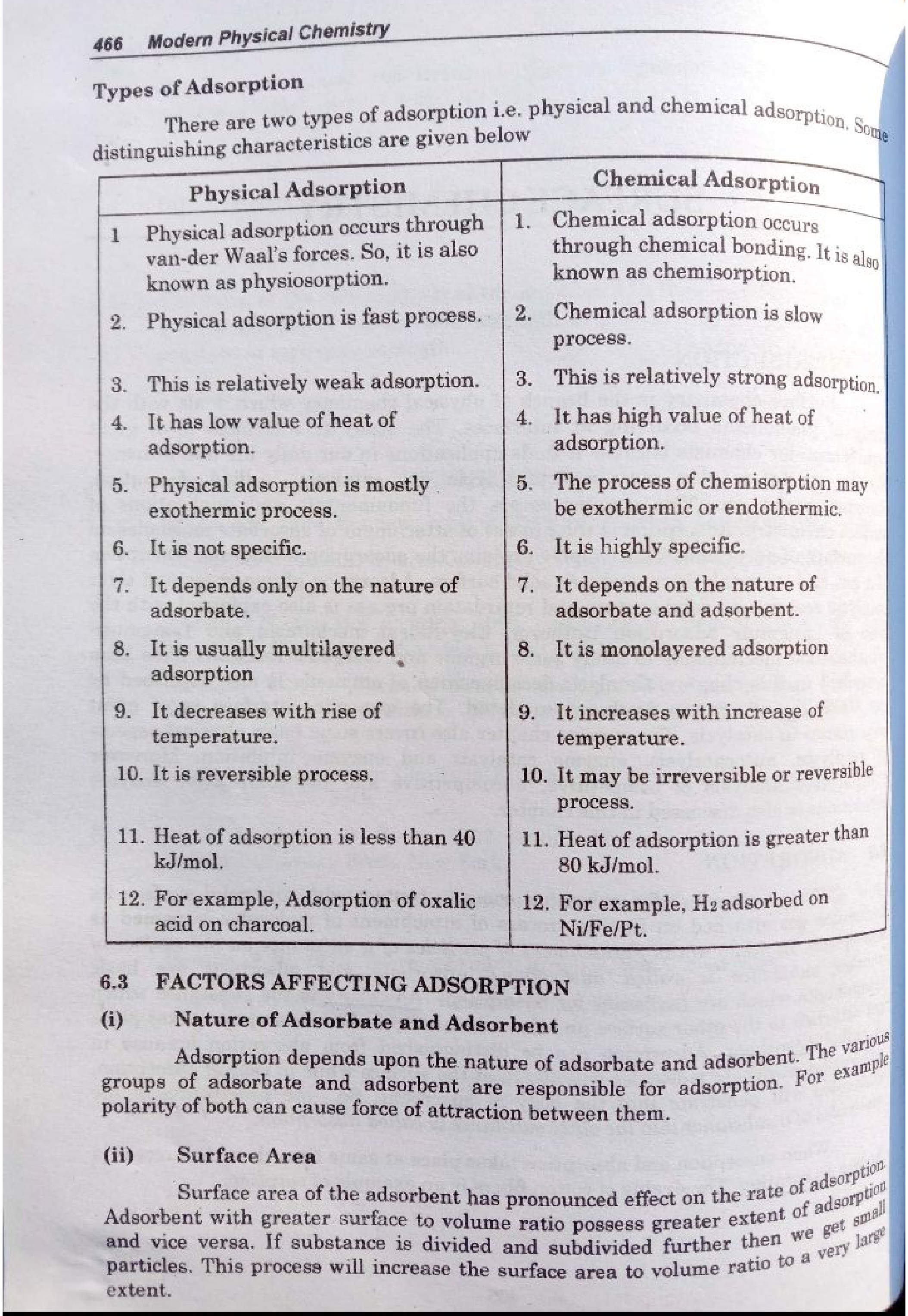
6.1 INTRODUCTION

Surface chemistry is the branch of physical chemistry which deals with the study of phenomena occurring at interfaces. The study of interfaces is of great significance for chemists because it finds applications in our daily life and industry. Mainly, surfaces play an important role in catalysis, colloid formation, chromatography etc. This chapter covers the fundamentals and applications of surface chemistry. Adsorption is the process of attachment of adsorbate molecules on the surface of adsorbent. This chapter explains the adsorption isotherms, adsorption of a gas and its catalytic reaction on solid surface. Adsorption of two gases and their catalytic reaction on solid surface and retardation process is also explained with the help of Langmuir adsorption isotherm. Eley-Rideal mechanism and Langmuir-Hinshelwood mechanisms to study some organic and inorganic reactions have been described in this chapter. Catalytic decomposition of ammonia is also described by the Tempkin adsorption isotherm in detail. The gas-solid interface is of great importance in catalysis. The current chapter also covers some basic physical aspects of catalysis, autocatalysis, enzyme catalysis and enzyme inhibition. Moreover comparative analysis of competitive, uncompetitive and non-competitive enzyme inhibitions is also discussed in this chapter.

6.2 ADSORPTION

When molecules of a substance come in contact with any solid surface its molecules get attached on it, this process of attachment of molecules is named as adsorption. In other words, "*attachment of particles of a substance on the surface of another substance is called adsorption.*" Adsorbate and adsorbent are basic components which are necessary for adsorption. Adsorbate is the substance which get attached to the other surface and the substance on which adsorption takes place is called adsorbent. Adsorption can be distinguished from absorption because in adsorption adsorbate molecules will attach at the surface while in case of absorption, molecules will penetrate into the body of adsorbent. So, "*the penetration of the molecules of a substance into the other substance is called absorption.*"

When adsorption and absorption takes place at same time then the process is known as sorption. The dyeing of cotton fibers is an example of sorption.



Types of Adsorption

There are two types of adsorption i.e. physical and chemical adsorption. Some distinguishing characteristics are given below

Physical Adsorption	Chemical Adsorption
1 Physical adsorption occurs through van-der Waal's forces. So, it is also known as physiosorption.	1. Chemical adsorption occurs through chemical bonding. It is also known as chemisorption.
2. Physical adsorption is fast process.	2. Chemical adsorption is slow process.
3. This is relatively weak adsorption.	3. This is relatively strong adsorption.
4. It has low value of heat of adsorption.	4. It has high value of heat of adsorption.
5. Physical adsorption is mostly exothermic process.	5. The process of chemisorption may be exothermic or endothermic.
6. It is not specific.	6. It is highly specific.
7. It depends only on the nature of adsorbate.	7. It depends on the nature of adsorbate and adsorbent.
8. It is usually multilayered adsorption	8. It is monolayered adsorption
9. It decreases with rise of temperature.	9. It increases with increase of temperature.
10. It is reversible process.	10. It may be irreversible or reversible process.
11. Heat of adsorption is less than 40 kJ/mol.	11. Heat of adsorption is greater than 80 kJ/mol.
12. For example, Adsorption of oxalic acid on charcoal.	12. For example, H_2 adsorbed on Ni/Fe/Pt.

6.3 FACTORS AFFECTING ADSORPTION

(i) Nature of Adsorbate and Adsorbent

Adsorption depends upon the nature of adsorbate and adsorbent. The various groups of adsorbate and adsorbent are responsible for adsorption. For example polarity of both can cause force of attraction between them.

(ii) Surface Area

Surface area of the adsorbent has pronounced effect on the rate of adsorption. Adsorbent with greater surface to volume ratio possess greater extent of adsorption and vice versa. If substance is divided and subdivided further then we get small particles. This process will increase the surface area to volume ratio to a very large extent.

(iii) Temperature

Temperature affects the process of adsorption. For example in most cases chemical adsorption increases with the increase of temperature, while physical adsorption decreases with the increase of temperature.

(iv) Pressure/Concentration

Dynamic equilibrium exists between the adsorbed and desorbed gas molecules during adsorption process. So, according to Le-Chatlier's principle increase in pressure leads to higher rate of adsorption. When pressure is decreased it causes desorption.

6.4 ADSORPTION ISOTHERMS

Adsorption of a substance on the surface of another substance can be investigated under various conditions of temperature and pressure but in most studies relation between extent of adsorption and equilibrium pressure has been explored. When a gas starts to adsorb on a surface, initially its rate of desorption depends upon number of molecules adsorbed. With the increase of number of molecules adsorbed, rate of desorption increases. *"When rate of adsorption becomes equal to the rate of desorption this state is called dynamic equilibrium."* At dynamic equilibrium, the pressure is called equilibrium pressure. The process of adsorption and desorption in a close vessel is shown in Fig. 6.1 (a) at equilibrium. *"The relation between extent of adsorption and equilibrium pressure at constant temperature is called adsorption isotherm."*

6.4.1 Freundlich Adsorption Isotherm

Freundlich gave an empirical relation between extent of adsorption and pressure of gas at constant temperature in the form of an empirical equation which is given below

$$\frac{x}{m} = kP^{1/n} \qquad (6.1)$$

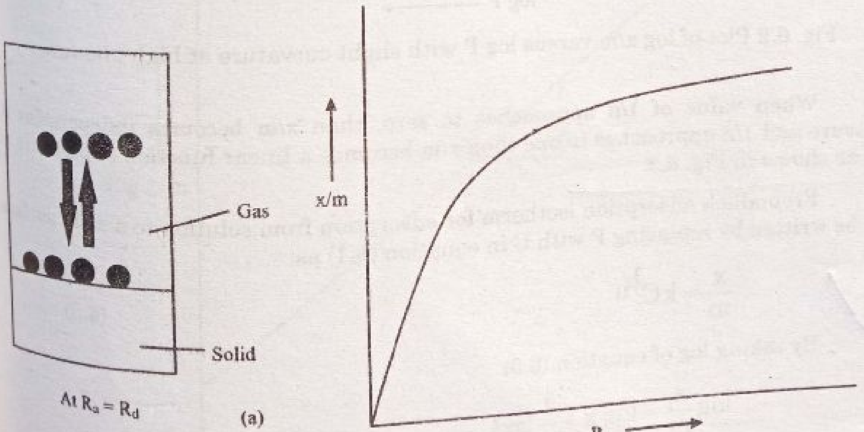


Fig. 6.1 (a) Adsorption desorption equilibrium
(b) x/m as a function of pressure of a gas at constant temperature

Where, P is the equilibrium pressure and x/m is the extent of adsorption i.e. amount of adsorbate adsorbed per unit mass of adsorbent. k and n are empirical constants which depend upon the nature of gas, solid and temperature, n is the dimensionless quantity but k has dimension of inverse of pressure. According to equation (6.1) extent of adsorption is a function of equilibrium pressure of gas as shown in Fig. 6.1 (b).

Equation (6.1) can be written in the form of equation of straight line as

$$\log\frac{x}{m}=\frac{1}{n}\log P+\log k \qquad (6.2)$$

According to equation (6.2) log (x/m) is a linear function of logP whose slope and intercept are 1/n and log k respectively as shown in Fig. 6.2. This plot can be used for the determination of values of empirical constants n and k.

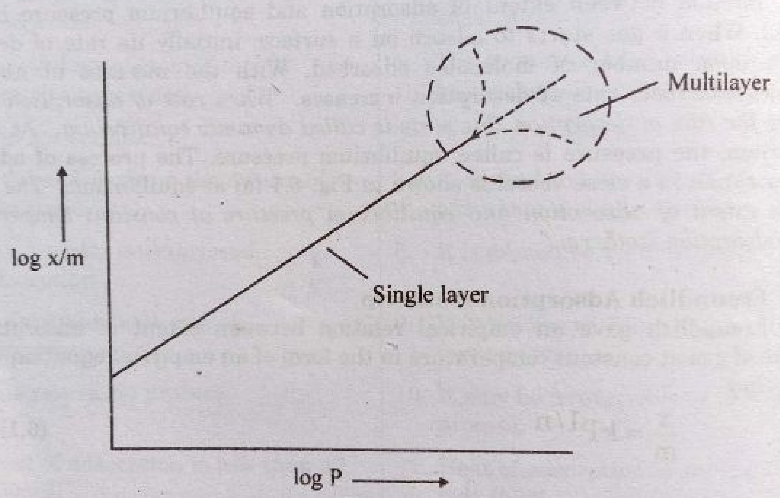


Fig. 6.2 Plot of log x/m versus log P with slight curvature at high pressure

When value of 1/n approaches to zero, then x/m becomes independent of pressure and 1/n approaches to one then x/m becomes a linear function of pressure of gas as shown in Fig. 6.3.

Freundlich adsorption isotherm for adsorption from solution to a solid surface can be written by replacing P with C in equation (6.1) as

$$\frac{x}{m}=kC^{1/n} \qquad (6.3)$$

By taking log of equation (6.3)

$$\log\frac{x}{m}=\log k+\frac{1}{n}\log C$$

This equation can be used to study the adsorption of toxic material on biosorbent in aqueous medium. Water purification can be done by suitable adsorbent using this equation. The value of n and k can be determined using plot as shown in Fig. 6.4.

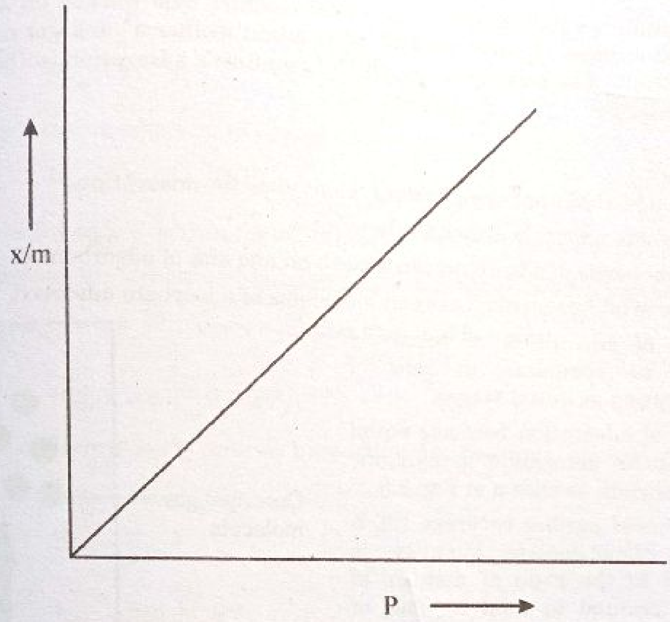


Fig. 6.3 Plot of x/m as a function of pressure when n = 1

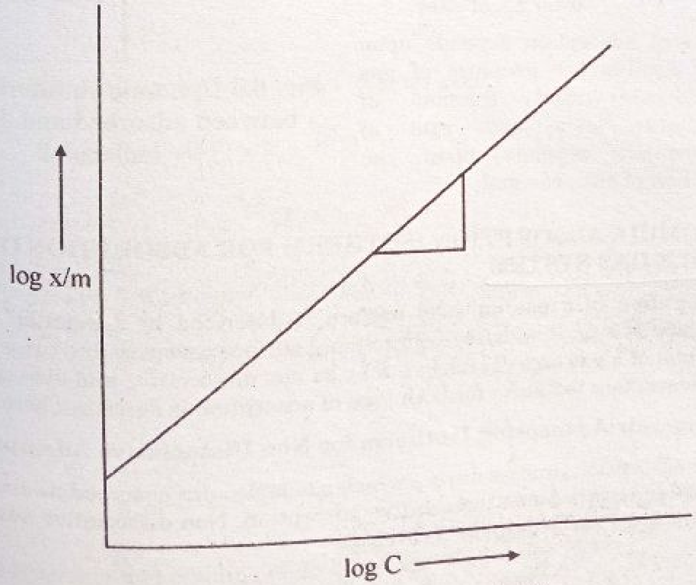


Fig. 6.4 Plot of log x/m versus log C

6.4.2 Langmuir's Adsorption Isotherm

Langmuir was an American physical chemist who worked on adsorption of gases on solid surface. He also derived "adsorption isotherm" and got noble prize in chemistry in 1932. The postulates on which Langmuir's adsorption isotherm is based are given below.

Postulates

(i) Each adsorbent has specific equivalent sites for adsorption.

(ii) Adsorbate molecule attach to these sites.

(iii) One molecule of adsorbate can adsorb on one site of adsorbent.

(iv) There is no interaction between molecules of adsorbate adsorbed.

(v) Rate of adsorption is relatively high as compared to rate of desorption at initial stages.

(vi) Rate of adsorption becomes equal to rate of desorption at dynamic equilibrium as shown in Fig. 6.5.

(vii) Fractional surface coverage (θ), a new dimensionless quantity is equal to the ratio of number of sites covered to total number of sites i.e.

$$\theta = \frac{\text{no. of sites occupied}}{\text{total no. of sites}}$$

(viii) Rate of adsorption depends upon the equilibrium pressure of gas (adsorbate) and fraction of available sites and rate of desorption depends upon the fraction of sites covered.

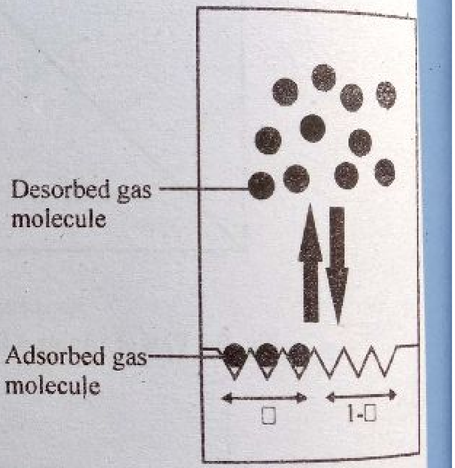


Fig. 6.5 Dynamic equilibrium exists between adsorbed and desorbed molecules

6.5 LANGMUIR ADSORPTION ISOTHERM FOR ADSORPTION OF SINGLE GAS SYSTEM

Adsorption of a gas on solid surface is described by Langmuir adsorption isotherm which is a relation between fractional surface coverage and pressure of gas. The adsorption of a gas on solid surface may be non dissociative and dissociative. The Langmuir adsorption isotherm for both type of adsorption is described here.

6.5.1 Langmuir Adsorption Isotherm for Non Dissociative Adsorption

The adsorption process during which gas molecules adsorbed as such without any dissociation is called non dissociative adsorption. Non dissociative adsorption of hydrogen on a solid surface can be written as

$$H_{2(gas)} \leftrightarrow H_{2(Ads)}$$

Rate of adsorption of a gas is directly proportional to pressure and fraction of unoccupied sites i.e.

$$R_{Ads} \propto P_A \qquad (6.4)$$

$$R_{Ads} \propto (1-\theta) \qquad (6.5)$$

On combining equation (6.4) and (6.5)

$$R_{Ads} = k_{Ads}(1-\theta)P_A \qquad (6.6)$$

k_{ads} is the rate constant for adsorption.

According to Arrhenius equation k_{ads} is the function of temperature and can be written as $k_{Ads} = b_1 e^{-\frac{E_{Ads}}{RT}}$. Then equation (6.6) will become

$$R_{Ads} = b_1 e^{-\frac{E_{Ads}}{RT}}(1-\theta)P_A \qquad (6.7)$$

Rate of desorption is directly proportional to fractional surface coverage i.e.

$$R_{Des} \propto \theta$$

$$R_{Des} = k_{Des}\theta$$

$$k_{Des} = b_2 e^{-\frac{E_{Des}}{RT}}.\theta \qquad (6.8)$$

At dynamic equilibrium, rate of adsorption becomes equal to the rate of desorption. So,

$$R_{Ads} = R_{Des}$$

By comparing equation (6.7) and (6.8) we get,

$$b_1 e^{-\frac{E_{Ads}}{RT}}(1-\theta)P_A = b_2 e^{-\frac{E_{Des}}{RT}}.\theta$$

$$b_1 e^{-\frac{E_{Ads}}{RT}}P_A - b_1 e^{-\frac{E_{Ads}}{RT}}\theta P_A = b_2 e^{-\frac{E_{Des}}{RT}}.\theta$$

$$b_1 e^{-\frac{E_{Ads}}{RT}}P_A = b_1 e^{-\frac{E_{Ads}}{RT}}\theta P_A + b_2 e^{-\frac{E_{Des}}{RT}}\theta$$

$$b_1 e^{-\frac{E_{Ads}}{RT}}P_A = \theta\left\{b_1 e^{-\frac{E_{Ads}}{RT}}P_A + b_2 e^{-\frac{E_{Des}}{RT}}\right\}$$

$$\theta = \frac{b_1 e^{-\frac{E_{Ads}}{RT}}P_A}{b_2 e^{-\frac{E_{Des}}{RT}} + b_1 e^{-\frac{E_{Ads}}{RT}}P_A}$$

Multiplying and dividing right hand side of equation by $b_2 e^{-\frac{E_{Des}}{RT}}$

$$\theta = \frac{b_1 e^{-\frac{E_{Ads}}{RT}} P_A / b_2 e^{-\frac{E_{Des}}{RT}}}{1 + \dfrac{b_1 e^{-\frac{E_{Ads}}{RT}} . P_A}{b_2 e^{-\frac{E_{Des}}{RT}}}}$$

$$\theta = \frac{\dfrac{b_1}{b_2} e^{\frac{E_{Des}}{RT}} e^{-\frac{E_{Ads}}{RT}} P_A}{1 + \dfrac{b_1}{b_2} e^{\frac{E_{Des}}{RT}} e^{-\frac{E_{Ads}}{RT}} P_A}$$

$$\theta = \frac{\left(\dfrac{b_1}{b_2}\right) e^{\frac{E_{Des} - E_{Ads}}{RT}} P_A}{1 + \left(\dfrac{b_1}{b_2}\right) e^{\frac{E_{Des} - E_{Ads}}{RT}} P_A}$$

$$\theta = \frac{\left(\dfrac{b_1}{b_2}\right) e^{\frac{-(E_{Ads} - E_{Des})}{RT}} P_A}{1 + \left(\dfrac{b_1}{b_2}\right) e^{\frac{-(E_{Ads} - E_{Des})}{RT}} P_A} \tag{6.9}$$

And, $\Delta H_{Ads} = E_{Ads} - E_{Des}$ (6.10)

The quantity E_{Ads}-E_{Des} is the heat of adsorption as shown in energy profile in Fig. 6.6.

Putting value of (E_{Ads}– E_{Des}) from equation (6.10) into equation (6.9), we get

$$\theta = \frac{\left(\dfrac{b_1}{b_2}\right) e^{-\frac{\Delta H_{Ads}}{RT}} P_A}{1 + \left(\dfrac{b_1}{b_2}\right) e^{-\frac{\Delta H_{Ads}}{RT}} P_A}$$

$$\left(\frac{b_1}{b_2}\right) e^{-\frac{\Delta H_{Ads}}{RT}} = b$$

So, above equation becomes

$$\theta = \frac{bP_A}{1 + bP_A} \tag{6.11}$$

b is the adsorption coefficient which depends upon the nature of adsorbate and adsorbent, it is temperature dependent and its units are Pa^{-1}.

Equation (6.11) is a relation between fractional surface coverage and pressure of gas. According to equation (6.11) θ is a function of pressure of gas. Fig. 6.7 gives dependence of θ on pressure. The value of θ increases with the increase of pressure of gas for small range of pressure and it becomes independent of pressure at very high value of pressure. At this stage, all sites are occupied by gas molecules, that is why further increase of pressure has no effect on extent of adsorption.

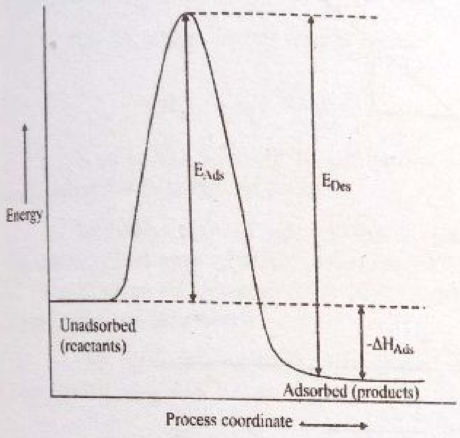


Fig. 6.6 Energy profile of adsorption and desorption processes

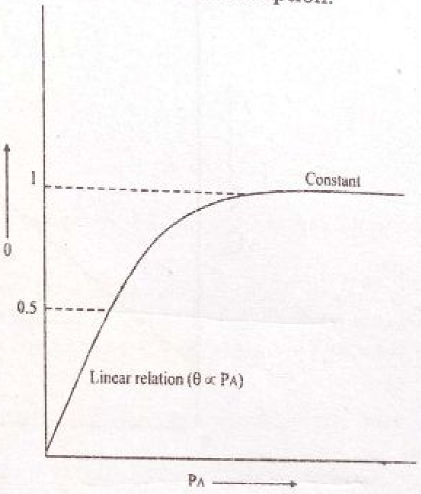


Fig. 6.7 θ as a function of pressure of gas A

Special Cases

(i) When P_A is low, then $1 + bP_A \approx 1$. So, equation (6.11) will become

$$\theta = bP_A$$

$$\theta \propto P_A.$$

So, θ is a linear function of P_A

(ii) When P_A is high, then $1 + bP_A \approx bP_A$. Then, equation (6.11) becomes

$$\theta = 1$$

So, fractional surface coverage is independent of available pressure. At this stage, adsorption or value only depends upon value of b. If weak adsorption occurs, then b has low value and if strong adsorption occurs, then value of b will be high.

By taking inverse of equation (6.11)

$$\frac{1}{\theta} = \frac{1 + bP_A}{bP_A}$$

$$\frac{1}{\theta} = \frac{1}{bP_A} + 1$$

$$\frac{1}{\theta} = \left(\frac{1}{b}\right)\left(\frac{1}{P_A}\right) + 1$$

This is an equation of straight line with intercept 1 and slope 1/b.

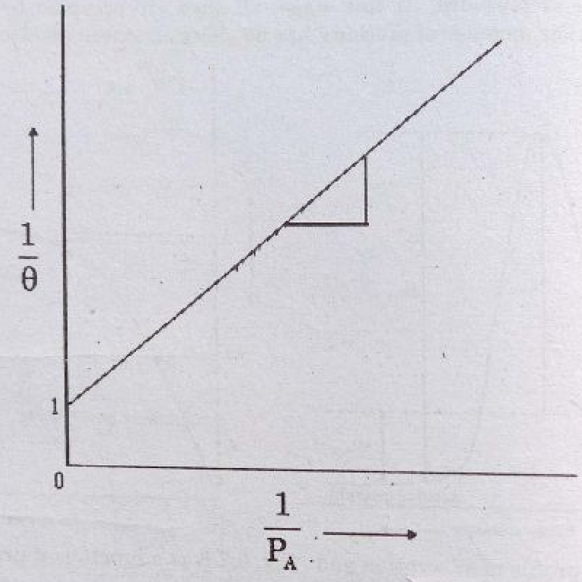


Fig. 6.8 Plot of 1/θ versus 1/P_A

Fig. 6.8 shows that 1/θ is directly proportional to 1/P_A. From the slope of this graph, value of b can be determined.

6.5.2 Langmuir Adsorption Isotherm for Dissociative Adsorption of a gas

The adsorption process during which dissociation of gas molecules takes place is called dissociative adsorption and for dissociative adsorption rate of adsorption is directly proportional to pressure and square of fraction of vacant sites of adsorbent i.e.

$$R_{Ads} \propto (1-\theta)^2$$

$$R_{Ads} \propto P_A$$

On combining above both equations we get,

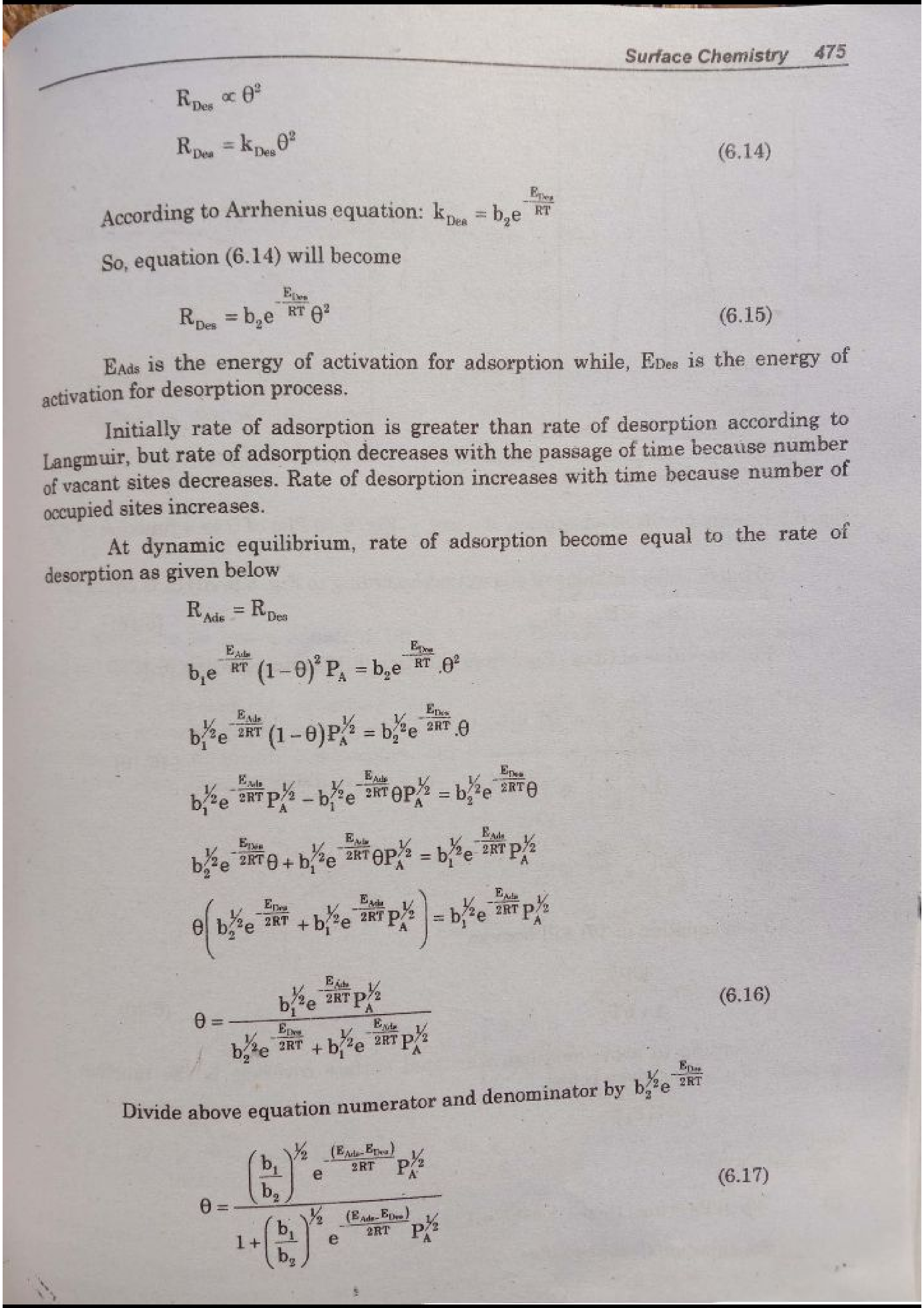
$$R_{Ads} = k_{Ads}(1-\theta)^2 P_A \qquad (6.12)$$

According to Arrhenius equation: $k_{Ads} = b_1 e^{-\frac{E_{Ads}}{RT}}$

So, equation (6.12) becomes

$$R_{Ads} = b_1 e^{-\frac{E_{Ads}}{RT}} P_A (1-\theta)^2 \qquad (6.13)$$

Rate of desorption is directly proportional to square of fractional surface coverage because two vacant sites are formed when a molecule of desorbed gas formed from adsorbed gas. It means it is second order reaction. Thus



$$R_{Des} \propto \theta^2$$

$$R_{Des} = k_{Des}\theta^2 \qquad (6.14)$$

According to Arrhenius equation: $k_{Des} = b_2 e^{-\frac{E_{Des}}{RT}}$

So, equation (6.14) will become

$$R_{Des} = b_2 e^{-\frac{E_{Des}}{RT}}\theta^2 \qquad (6.15)$$

E_{Ads} is the energy of activation for adsorption while, E_{Des} is the energy of activation for desorption process.

Initially rate of adsorption is greater than rate of desorption according to Langmuir, but rate of adsorption decreases with the passage of time because number of vacant sites decreases. Rate of desorption increases with time because number of occupied sites increases.

At dynamic equilibrium, rate of adsorption become equal to the rate of desorption as given below

$$R_{Ads} = R_{Des}$$

$$b_1 e^{-\frac{E_{Ads}}{RT}}(1-\theta)^2 P_A = b_2 e^{-\frac{E_{Des}}{RT}}.\theta^2$$

$$b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}(1-\theta)P_A^{1/2} = b_2^{1/2} e^{-\frac{E_{Des}}{2RT}}.\theta$$

$$b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}P_A^{1/2} - b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}\theta P_A^{1/2} = b_2^{1/2} e^{-\frac{E_{Des}}{2RT}}\theta$$

$$b_2^{1/2} e^{-\frac{E_{Des}}{2RT}}\theta + b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}\theta P_A^{1/2} = b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}P_A^{1/2}$$

$$\theta\left(b_2^{1/2} e^{-\frac{E_{Des}}{2RT}} + b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}P_A^{1/2}\right) = b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}P_A^{1/2}$$

$$\theta = \frac{b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}P_A^{1/2}}{b_2^{1/2} e^{-\frac{E_{Des}}{2RT}} + b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}P_A^{1/2}} \qquad (6.16)$$

Divide above equation numerator and denominator by $b_2^{1/2} e^{-\frac{E_{Des}}{2RT}}$

$$\theta = \frac{\left(\frac{b_1}{b_2}\right)^{1/2} e^{-\frac{(E_{Ads}-E_{Des})}{2RT}} P_A^{1/2}}{1+\left(\frac{b_1}{b_2}\right)^{1/2} e^{-\frac{(E_{Ads}-E_{Des})}{2RT}} P_A^{1/2}} \qquad (6.17)$$

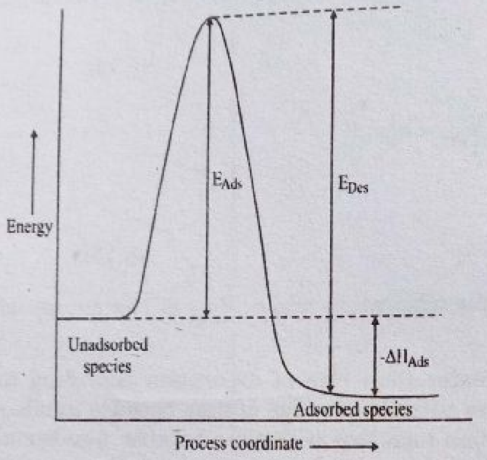


Fig. 6.9 Energy profile of adsorption of a gas

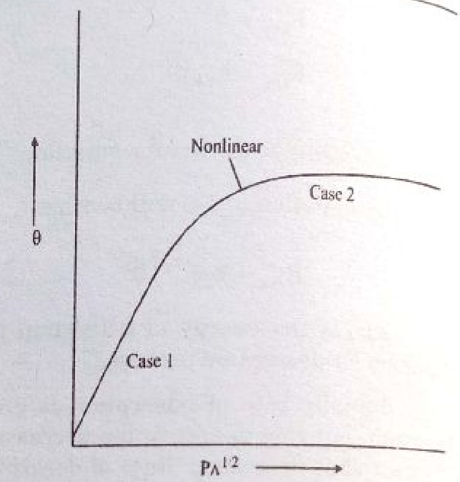


Fig. 6.10 Plot of θ as a function of $P_A^{1/2}$

ΔH_{Ads} denotes enthalpy of adsorption according to Fig. 6.9. ΔH_{Ads} is equal to

$$\Delta H_{Ads} = E_{Ads} - E_{Des} \tag{6.18}$$

Putting value of ($E_{Ads} - E_{Des}$) from equation (6.18) into equation (6.17)

$$\theta = \frac{\left(\frac{b_1}{b_2}\right)^{1/2} e^{-\frac{\Delta H_{Ads}}{2RT}} P_A^{1/2}}{1 + \left(\frac{b_1}{b_2}\right)^{1/2} e^{-\frac{\Delta H_{Ads}}{2RT}} P_A^{1/2}} \tag{6.19}$$

If, $\left(\frac{b_1}{b_2}\right)^{1/2} e^{-\frac{\Delta H_{Ads}}{2RT}} = b'$

Then equation (6.19) will become

$$\theta = \frac{b' P_A^{1/2}}{1 + b' P_A^{1/2}} \tag{6.20}$$

According to above relation, fractional surface coverage is the function of pressure of gas A as given below

$$\theta = f(P_A)$$

Special Cases

(i) When P_A is low, then $1 + b P_A^{1/2} \approx 1$

So, equation (6.20) becomes

$$\theta = b'P_A^{1/2}$$

$$\theta \propto P_A^{1/2}$$

It means θ is directly proportional to $P_A^{1/2}$ (Fig. 6.10).

(ii) When P_A is high, then $1 + bP_A^{1/2} \approx P_A^{1/2}$. So, equation (6.20) becomes

$$\theta = 1$$

It means θ is independent of pressure when P_A is high (Fig. 6.10).

By taking inverse of equation (6.20)

$$\frac{1}{\theta} = \frac{1 + b'P_A^{1/2}}{b'P_A^{1/2}}$$

$$\frac{1}{\theta} = \frac{1}{b'P_A^{1/2}} + 1$$

According to above equation 1/θ is a linear function of $1/P_A^{1/2}$ whose slope equal to 1/b', and intercept equal to 1 as shown in Fig. 6.11.

On comparison of equations (6.11) and (6.20) of non-dissociative and dissociative adsorption respectively, it is concluded that θ is more dependent on pressure for non dissociative adsorption but θ is less dependent on pressure for dissociative adsorption as shown in Fig. 6.12.

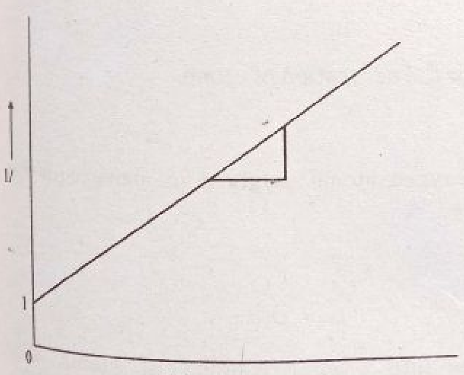


Fig. 6.11 Plot of 1/θ versus $1/P_A^{1/2}$ with intercept 1

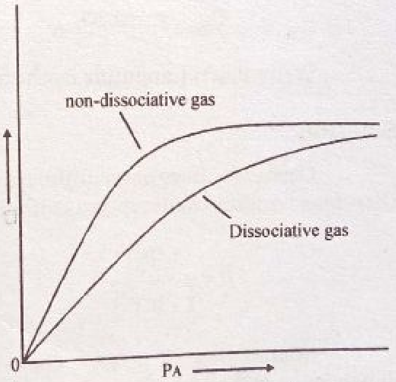


Fig. 6.12 Plot showing dependence of θ on P_A for dissociative and non-dissociative adsorption

Limitations

The Langmuir adsorption isotherm gives a quantitative explanation of the adsorption. The mechanism of chemical adsorption can also be explained with the help of Langmuir equation. The Langmuir adsorption isotherm gives a satisfactory theoretical explanation of a large number of experimental results. But it also has some limitations as Langmuir adsorption isotherm assumes that surface is capable of adsorbing one molecule thick layer. But in actual practice, there are chances of multilayer formation. According to this theory, the saturation value of adsorption should be independent of temperature. But experiments show that saturation value decreases with the rise of temperature. This theory holds good only at low pressure.

Example 6.1

Adsorption of ozone on solid surface takes place according to following scheme

$$O_{3(gas)} \rightleftharpoons O_{Ads} + O_{2(Ads)}$$

Write down Langmuir adsorption isotherm for the adsorption.

Solution

According to the reaction given above, ozone is dissociated into two species, therefore Langmuir isotherm for the adsorption of ozone will be

$$\theta = \frac{b'P_{O_3}^{1/2}}{1 + b'P_{O_3}^{1/2}}$$

Example 6.2

Adsorption of ozone on solid surface takes place according to following scheme

$$O_{3(gas)} \rightleftharpoons 3O_{(Ads)}$$

Write down Langmuir isotherm for the adsorption of ozone.

Solution

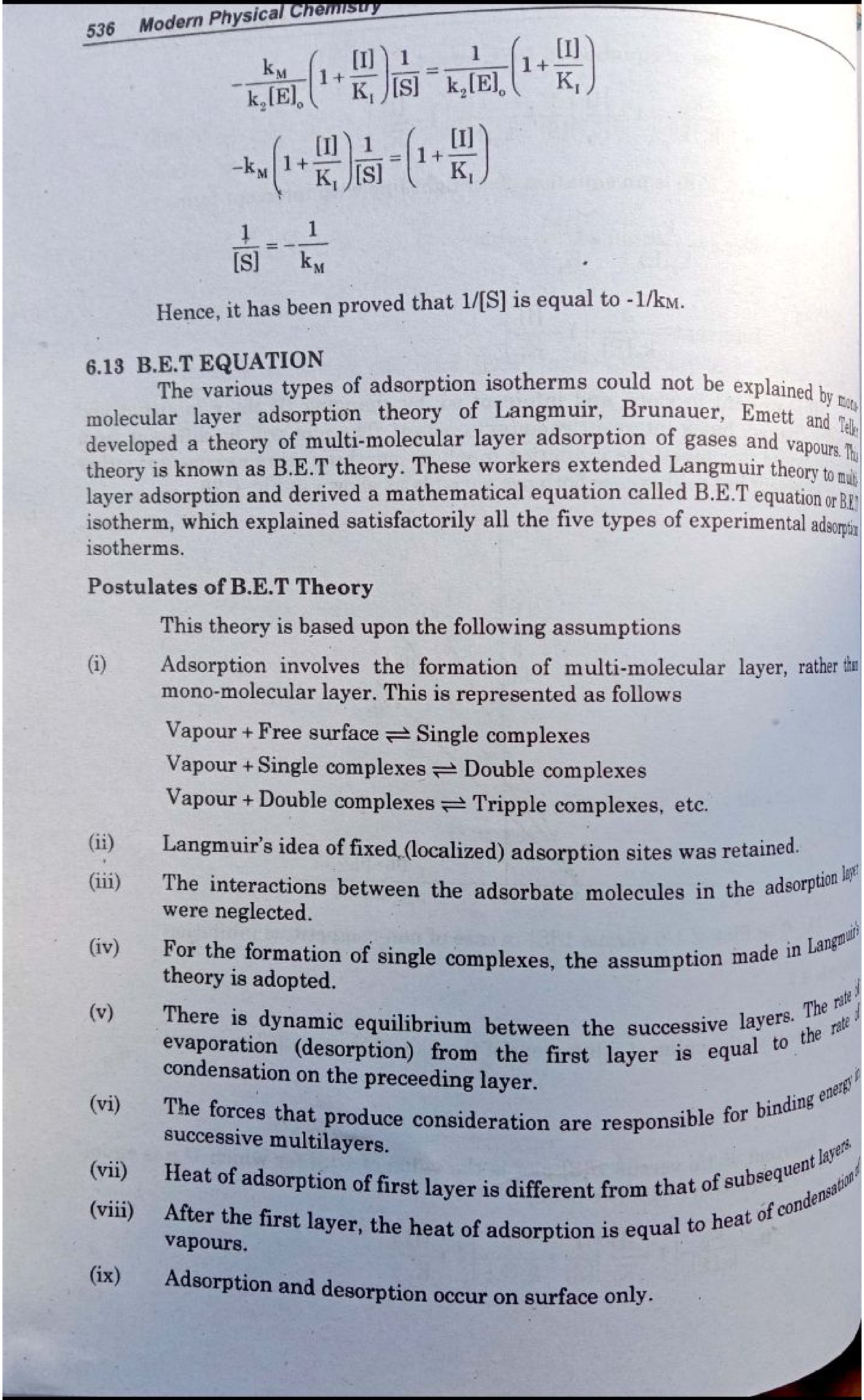
Ozone is dissociated into three oxygen atoms as given in above equation, therefore Langmuir adsorption isotherm is

$$\theta = \frac{b''P_{O_3}^{1/3}}{1 + b''P_{O_3}^{1/3}}$$

Comments: If a gas dissociates into greater number of atoms, then dependence of θ on pressure of gas decreases.

6.6 APPLICATION OF LANGMUIR ADSORPTION ISOTHERM FOR SINGLE SYSTEM

The Langmuir adsorption isotherm for single system can be used for the determination of isosteric enthalpy of adsorption (ΔH_θ) and for the study of catalytic reaction of gas on solid surface.



$$-\frac{k_M}{k_2[E]_o}\left(1+\frac{[I]}{K_I}\right)\frac{1}{[S]}=\frac{1}{k_2[E]_o}\left(1+\frac{[I]}{K_I}\right)$$

$$-k_M\left(1+\frac{[I]}{K_I}\right)\frac{1}{[S]}=\left(1+\frac{[I]}{K_I}\right)$$

$$\frac{1}{[S]}=-\frac{1}{k_M}$$

Hence, it has been proved that $1/[S]$ is equal to $-1/k_M$.

6.13 B.E.T EQUATION

The various types of adsorption isotherms could not be explained by mono-molecular layer adsorption theory of Langmuir, Brunauer, Emett and Teller developed a theory of multi-molecular layer adsorption of gases and vapours. This theory is known as B.E.T theory. These workers extended Langmuir theory to multi-layer adsorption and derived a mathematical equation called B.E.T equation or B.E.T isotherm, which explained satisfactorily all the five types of experimental adsorption isotherms.

Postulates of B.E.T Theory

This theory is based upon the following assumptions

(i) Adsorption involves the formation of multi-molecular layer, rather than mono-molecular layer. This is represented as follows

Vapour + Free surface ⇌ Single complexes
Vapour + Single complexes ⇌ Double complexes
Vapour + Double complexes ⇌ Tripple complexes, etc.

(ii) Langmuir's idea of fixed (localized) adsorption sites was retained.

(iii) The interactions between the adsorbate molecules in the adsorption layer were neglected.

(iv) For the formation of single complexes, the assumption made in Langmuir's theory is adopted.

(v) There is dynamic equilibrium between the successive layers. The rate of evaporation (desorption) from the first layer is equal to the rate of condensation on the preceeding layer.

(vi) The forces that produce consideration are responsible for binding energy in successive multilayers.

(vii) Heat of adsorption of first layer is different from that of subsequent layers.

(viii) After the first layer, the heat of adsorption is equal to heat of condensation of vapours.

(ix) Adsorption and desorption occur on surface only.

Statement of B.E.T Equation

On the basis of above postulates, Brunauer, Emmett and Teller derived the following equation

$$\frac{p}{V(p^\circ - p)} = \frac{1}{V_m C} + \left(\frac{C-1}{V_m C}\right)\frac{p}{p^\circ} \qquad (6.159)$$

This equation is called B.E.T equation. In this equation

Here V is volume, reduced to standard conditions of the gas adsorbed at pressure p and temperature T, p^o is saturated vapour pressure of adsorbate (gas or vapour) at temperature T and V_m is volume of gas, reduced to standard conditions (i.e. at NTP), adsorbed to form a saturated monolayer per gram of the adsorbent. While C is a constant equal to $e^{(E_1 - E_L)/RT}$ at any given temperature. Here E_1 is heat of adsorption of first layer, E_L is heat of condensation of the gas and E_1 E_L is net heat of adsorption.

Derivation of B.E.T Equation

If at any time θ_1, θ_2 and θ_3 ..... are the fractions of the surface covered by single, double and triple complexes respectively, then the extent of adsorption is given by the volume of the gas adsorbed on the surface. Then

$$V = V_m(\theta_1 + 2\theta_2 + 3\theta_3 + \ldots) \qquad (6.160)$$

Where V_m is the volume of the adsorbed gas to form unimolecular layer or it is the capacity for one dense layer.

Since equilibrium exists between different phases, hence expressions for the equilibrium constants of the reactions are

Fraction of surface covered α Naked surface × Number of molecules striking per unit area

Fraction of surface covered α $(1 \quad \theta) \times P$

Fraction of surface covered α $\theta_o \times P$

So

$$\theta_1 = K_1 P \theta_o$$

$$K_1 = \frac{\theta_1}{P\theta_o} \qquad (6.161)$$

Similarly

$$K_2 = \frac{\theta_2}{P\theta_1} \qquad (6.162)$$

$$K_3 = \frac{\theta_3}{P\theta_2} \qquad (6.163)$$

Where θ_o is the fraction of free surface at equilibrium. The difference between K_1 and K_2 is usually large because K_1 is very greater than K_2. This is due to sharp reduction in adsorbate-adsorbent interaction with increase in distance. The difference between K_2 and K_3 or K_3 and K_4 are very small, hence it is assumed that

$$K_2 = K_3 = K_L \tag{6.164}$$

Where K_L is the equilibrium constant for saturated vapour-liquid transition and is given by

$$K_L = \frac{1}{P_o} \tag{6.165}$$

Thus from equations (6.161) to (6.164), we have

$$\theta_2 = K_2P\theta_1 = K_LP\theta_1 = \left(\frac{P}{P^o}\right)\theta_1$$

$$\theta_3 = K_3P\theta_2 = K_LP\theta_2 = \left(\frac{P}{P^o}\right)\left(\frac{P}{P^o}\right)\theta_1 = \left(\frac{P}{P^o}\right)^2\theta_1$$

....

....

$$\theta_i = K_iP\theta_{i-1} = K_LP\theta_{i-1} = \left(\frac{P}{P^o}\right)^{i-1}\theta_1 \tag{6.166}$$

Using equation (6.166), equation (6.160) is modified as

$$V = V_m\left(\theta_1 + \left(\frac{P}{P^o}\right)^2\theta_1 + \left(\frac{P}{P^o}\right)^3\theta_1 + \ldots\right)$$

$$V = V_m\theta_1\left(1 + \left(\frac{P}{P^o}\right)^2 + \left(\frac{P}{P^o}\right)^3 + \ldots\right)$$

$$V = V_mK_1P\theta_o\left(1 + \left(\frac{P}{P^o}\right)^2 + \left(\frac{P}{P^o}\right)^3 + \ldots\right) \tag{6.167}$$

Using binomial theorem, for values $P \le P_o$ we have

$$\left(1 + \left(\frac{P}{P^o}\right)^2 + \left(\frac{P}{P^o}\right)^3 + \ldots\right) = \frac{1}{\left(1 - \frac{P}{P^o}\right)^2}$$

Putting this value in equation (6.167) we have

$$V = V_m\left(\frac{K_1P\theta_o}{\left(1 - \frac{P}{P^o}\right)^2}\right) \tag{6.168}$$

The total coverage of the surface

$$\theta_o + \theta_1 + \theta_2 + \theta_3 + \ldots = 1$$

Putting values of θ_1, θ_2, θ_3 .... into above equation

$$\theta_o + K_1P\theta_o + \left(\frac{P}{P^o}\right)K_1P\theta_o + \left(\frac{P}{P^o}\right)^2 K_1P\theta_o + \ldots = 1$$

$$\theta_o\left(1 + K_1P + \left(\frac{P}{P^o}\right)K_1P + \left(\frac{P}{P^o}\right)^2 K_1P + \ldots\right) = 1$$

$$\theta_o\left(1 + K_1P\left(1 + \left(\frac{P}{P^o}\right) + \left(\frac{P}{P^o}\right)^2 + \ldots\right)\right) = 1$$

As $1 + r + r^2 + ... + \infty = \frac{1}{1-r}$, so above equation is modified as

$$\theta_o\left(1 + \frac{K_1P}{\left(1 - \frac{P}{P^o}\right)}\right) = 1 \qquad (6.169)$$

$$\theta_o\left(\frac{1 - \frac{P}{P^o} + K_1P}{1 - \frac{P}{P^o}}\right) = 1$$

$$\theta_o = \left(\frac{1 - \frac{P}{P^o}}{1 - \frac{P}{P^o} + K_1P}\right) \qquad (6.170)$$

Substituting the value of θ_o from equation (6.170) into (6.168)

$$V = V_m\left(\frac{K_1P\left(\frac{1 - \frac{P}{P^o}}{1 - \frac{P}{P^o} + K_1P}\right)}{\left(1 - \frac{P}{P^o}\right)^2}\right)$$

$$V = V_m\left(\frac{K_1P}{\left(1-\frac{P}{P^\circ}\right)\left(1-\frac{P}{P^\circ}+K_1P\right)}\right)$$

$$V = V_m\left(\frac{K_1P}{\left(1-\frac{P}{P^\circ}\right)\left(1+\frac{K_1PP^\circ-P}{P^\circ}\right)}\right)$$

$$V = V_m\left(\frac{K_1P}{\left(1-\frac{P}{P^\circ}\right)\left(1+\left(K_1P^\circ-1\right)\frac{P}{P^\circ}\right)}\right) \tag{6.171}$$

As $\quad K_1P = (K_1P)\frac{P^\circ}{P^\circ} = \frac{K_1}{K_L}\left(\frac{P}{P^\circ}\right) = c\left(\frac{P}{P^\circ}\right)$

and $\quad K_1P^\circ = \frac{K_1}{K_L} = c$

Putting value of K_1P and K_1P° into equation (6.171)

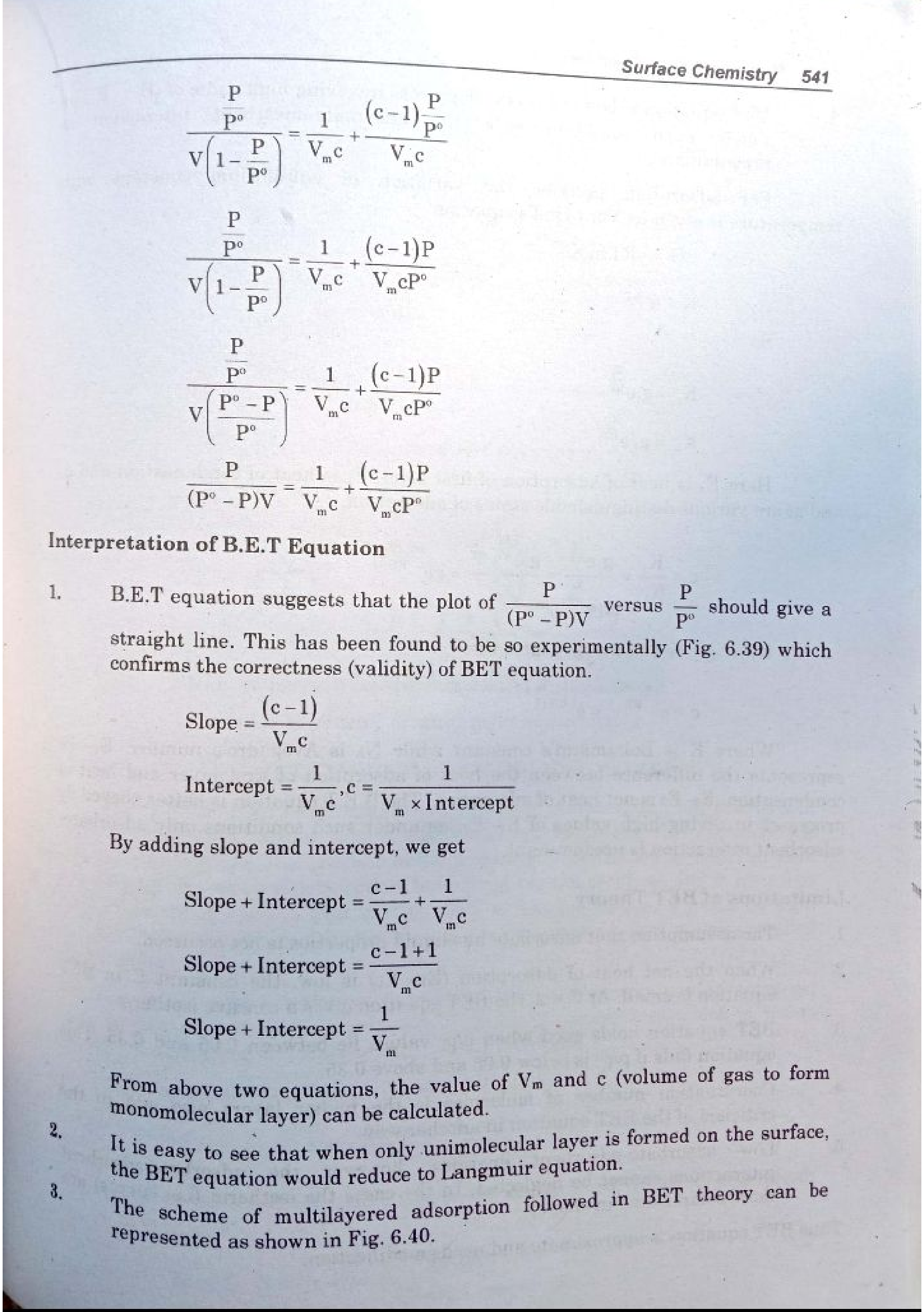
$$V = V_m\left(\frac{c\left(\frac{P}{P^\circ}\right)}{\left(1-\frac{P}{P^\circ}\right)\left(1+(c-1)\frac{P}{P^\circ}\right)}\right)$$

This is the B.E.T equation for adsorption. It involves vapour pressure (P), saturated vapour pressure (P°) at the temperature of the experiment, and two constants V_m and c. This equation can be rearranged as

$$V\left(1-\frac{P}{P^\circ}\right) = \frac{V_m c\left(\frac{P}{P^\circ}\right)}{\left(1+(c-1)\frac{P}{P^\circ}\right)}$$

$$\frac{1}{V\left(1-\frac{P}{P^\circ}\right)} = \frac{1+(c-1)\frac{P}{P^\circ}}{V_m c\left(\frac{P}{P^\circ}\right)}$$

$$\frac{\frac{P}{P^\circ}}{V\left(1-\frac{P}{P^\circ}\right)} = \frac{1+(c-1)\frac{P}{P^\circ}}{V_m c}$$



$$\frac{\frac{P}{P^\circ}}{V\left(1-\frac{P}{P^\circ}\right)}=\frac{1}{V_m c}+\frac{(c-1)\frac{P}{P^\circ}}{V_m c}$$

$$\frac{\frac{P}{P^\circ}}{V\left(1-\frac{P}{P^\circ}\right)}=\frac{1}{V_m c}+\frac{(c-1)P}{V_m cP^\circ}$$

$$\frac{\frac{P}{P^\circ}}{V\left(\frac{P^\circ-P}{P^\circ}\right)}=\frac{1}{V_m c}+\frac{(c-1)P}{V_m cP^\circ}$$

$$\frac{P}{(P^\circ-P)V}=\frac{1}{V_m c}+\frac{(c-1)P}{V_m cP^\circ}$$

Interpretation of B.E.T Equation

1. B.E.T equation suggests that the plot of $\frac{P}{(P^\circ-P)V}$ versus $\frac{P}{P^\circ}$ should give a straight line. This has been found to be so experimentally (Fig. 6.39) which confirms the correctness (validity) of BET equation.

$$\text{Slope}=\frac{(c-1)}{V_m c}$$

$$\text{Intercept}=\frac{1}{V_m c},\ c=\frac{1}{V_m\times \text{Intercept}}$$

By adding slope and intercept, we get

$$\text{Slope}+\text{Intercept}=\frac{c-1}{V_m c}+\frac{1}{V_m c}$$

$$\text{Slope}+\text{Intercept}=\frac{c-1+1}{V_m c}$$

$$\text{Slope}+\text{Intercept}=\frac{1}{V_m}$$

From above two equations, the value of V_m and c (volume of gas to form monomolecular layer) can be calculated.

2. It is easy to see that when only unimolecular layer is formed on the surface, the BET equation would reduce to Langmuir equation.

3. The scheme of multilayered adsorption followed in BET theory can be represented as shown in Fig. 6.40.

4. BET equation is better to obey by process involving high value of $(E_1\ E_L)$ as under such condition only the adsorbate-adsorbent interaction is predominant.

For adsorption process, the variation of equilibrium constant with temperature is given by Vont Hoff's equation

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

$$K = e^{-\frac{\Delta G}{RT}}$$

So

$$K_1 = g_1 e^{\frac{E_1}{RT}}$$

$$K_L = g_L e^{\frac{E_L}{RT}}$$

Here E_1 is heat of adsorption of first layer, E_L is heat of condensation and g_1 and g_2 are various distinguishable states of adsorption.

$$c = \frac{K_1}{K_L} = \frac{g_1 e^{\frac{E_1}{RT}}}{g_L e^{\frac{E_L}{RT}}} = \frac{g_1 e^{\frac{E_1}{RT} - \frac{E_L}{RT}}}{g_L} = g e^{\left(\frac{E_1 - E_L}{RT}\right)}$$

If we ignore the energy states then

$$c = e^{\left(\frac{E_1 - E_L}{RT}\right)} = e^{\left(\frac{E_1 - E_L}{KN_A T}\right)}$$

Where K is Boltzmann's constant while N_A is Avogadro's number. $E_1 - E_2$ represents the difference between the heat of adsorption of first layer and heat of condensation. $E_1 - E_2$ is net heat of adsorption. The B.E.T equation is better obeyed by processes involving high values of $E_1 - E_2$, as under such conditions only adsorbate-adsorbent interaction is predominant.

Limitations of BET Theory

1. The assumption that adsorbate has liquid properties is not occurred.
2. When the net heat of adsorption $(E_1 - E_L)$ is low, the constant C in BET equation is small. At $C < 2$, the BET equation gives a concave isotherm.
3. BET equation holds good when p/p^o values lie between 0.05 and 0.35. This equation fails if p/p^o is below 0.05 and above 0.35.
4. Coordination number of molecules is the higher layers also add to the criticism of the BET equation in another way.
5. Low adsorbate-adsorbent energies, however the adsorbate-adsorbent interactions cannot be neglected. In the cases the isotherm (i.e. curves) are more complicated in shape.

Thus BET equation is approximate and needs modification.

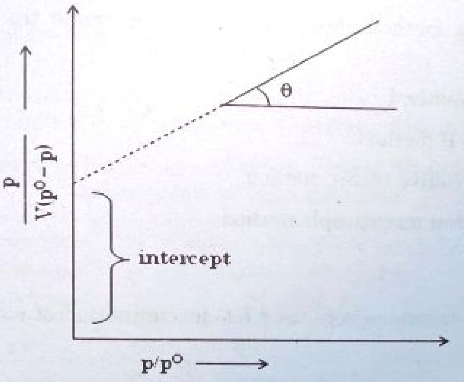


Fig. 6.39 Testing of BET equation

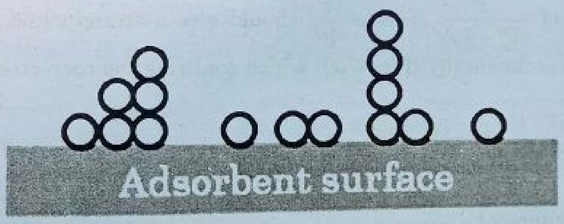


Fig. 6.40 Scheme of multi-layer adsorption

6.14 SURFACE AREA DETERMINATION OF SOLID ADSORBENTS

Generally the solid adsorbents which are used in adsorption are porous and used in powder form. So surface area of adsorbents gets increased. This enhances the magnitude of adsorption. The question of the surface area possessed by finely divided solid is not only important in adsorption, but also in contact catalysis and many other fields. BET isotherm showed that it is possible to use adsorption of gases by such materials for determination of their surface areas and thus finished a very powerful tool being widely used at present.

The porous solid adsorbents possess two types of surface areas: (A) external or outer surface area of porous particles and (B) inner surface area which is due to inner walls of capillaries and cracks in the porous particles.

The roughness factor of the catalyst is defined as

$$\text{Roughness factor} = \frac{\text{Total surface area}}{\text{Outer surface area}}$$

Hence (i) for smooth surface, roughness factor is unity and (ii) for rough surface, it is very high.

$$\text{Specific surface area} = \frac{\text{Surface area}}{\text{Mass of adsorbent}}$$

$$6\pi\eta r v_t = (\rho - \rho_m) x w^2 \left(\frac{4}{3}\pi r^3\right)$$

$$v_t = \frac{2(\rho - \rho_m) x w^2 r^2}{9\eta}$$

As v_t is the rate of change of distance with respect to time, the above equation can also be written as

$$\frac{dx}{dt} = \frac{2(\rho - \rho_m) x w^2 r^2}{9\eta}$$

Let the particle be at position x_1 and x_2 at time t_1 and t_2 respectively. Separating the variables in the above equation and integrating between the limits of time and the corresponding distance, we get

$$\int_{x_1}^{x_2} \frac{dx}{x} = \frac{2(\rho - \rho_m) w^2 r^2}{9\eta} \int_{t_1}^{t_2} dt$$

$$\ln \frac{x_2}{x_1} = \frac{2(\rho - \rho_m) w^2 r^2}{9\eta} (t_2 - t_1) \qquad (11.26)$$

Where x_1 and x_2 can be easily measured using optical microscope during centrifugation. Hence the value of r can be calculated using equation (11.26) if all other parameters are known.

(3) Microscopic Methods

Transmission electron microscopy (TEM) and Scanning electron microscopy can also be used to determine the size of droplets of emulsion.

(4) Scattering Methods

Dynamic light scattering, small angle neutron scattering and small angle x-ray scattering are also used to determine the droplet size.

11.10 SURFACTANTS: EMULSIFIERS

"The substance which lowers the interfacial tension between two liquids and is used to stabilize the emulsion by increasing its kinetic stability is named as emulsifier". These can be classified as: surfactant, lyophillic colloid, finely divided solid particles and polymeric materials. Surfactants are surface active substances which can be used as emulsifier due to their amphiphilic structure.

Classification of Surfactants

Surfactants can be classified according to polar head groups into two main classes.

(1) Ionic surfactants

(2) Non-ionic surfactants

(1) Ionic Surfactants

The surfactants that have the ability to dissociate in water are called ionic surfactants e.g.;

$$CH_3(CH_2)_{11}SO_4^- Na^+ \rightleftharpoons CH_3(CH_2)_{11}SO_4^- + Na^+$$

Sodium dodecyl sulfonate

$$CH_3(CH_2)_{11}NH_3^+Cl^- \rightleftharpoons CH_3(CH_2)_{11}NH_3^+ + Cl^-$$

Lauryl amine hydrochloride

Ionic surfactant is further divided into three classes.

(a) Anionic Surfactants

Anionic surfactants contain anionic functional group at their head e.g. sodium dodecyl benzene sulfonate.

$$CH_3(CH_2)_{11}C_6H_4SO_3^-Na^+ \rightleftharpoons CH_3(CH_2)_{11}C_6H_4SO_3^- + Na^+$$

(b) Cationic Surfactants

Cationic surfactants are those in which hydrophillic portion contain cationic functional group e.g.; trimethyl dodecyl ammonium chloride.

$$C_{12}H_{25}N^+(CH_3)_3Cl^- \rightleftharpoons C_{12}H_{25}N^+(CH_3)_3 + Cl^-$$

(c) Zwitterionic or Amphoteric Surfactants

The surfactant which contains a head with positive and negative charges is called amphoteric/zwiterionic surfactant e.g. dodecyl betaine [$C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$].

(2) Non–Ionic Surfactants

Non-ionic surfactants are those surfactants that have no charge group and can't be dissociated in water. Block copolymers of oxyethylene and oxybutylene are examples of non-ionic surfactants. Further non-ionic surfactants may be of two types either polymeric or non-polymeric surfactants.

11.11 PROPERTIES OF SURFACTANTS

Some important properties of the surfactants due to which they act as emulsifiers are discussed below

(1) Amphiphillic Structure

Surfactant molecule has amphiphillic structure, because it has a large hydrocarbons chain which is hydrophobic tail and hydrophilic head in nature as shown in Fig. 11.11.

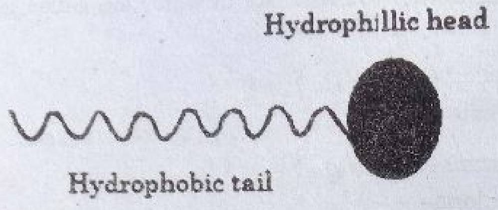


Fig. 11.11 Amphiphillic structure of surfactant.

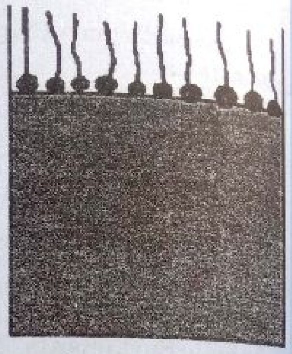


Fig. 11.12 Surfactant adsorption on air-water interfaces.

(2) Adsorption or Surface Activity

When surfactant is added into water it forms a layer at air-water interface by adsorption process as shown in Fig. 11.12. Surfactant adsorbs in such a way that its polar head is directed towards the aqueous phase and non-polar portion towards air phase and become adsorb on air-water interface.

(3) Reduction of Surface Tension

When surfactant adsorbs on the surface, then attraction on the surface atoms is balanced. Now downward force is balanced by upward force of surfactant. In this way, surfactant decreases the surface tension of liquid.

(4) Association or Micellization

"The process of micelle formation is called micellization". When a large quantity of surfactant is added in water after covering the whole air-water interface, the surfactant molecules will diffuse into the bulk material and they aggregate spontaneously to form a micelle as shown in Fig. 11.13.

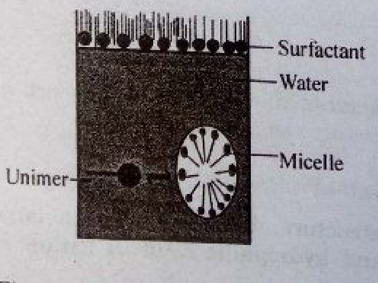


Fig. 11.13 Adsorption and micellization process

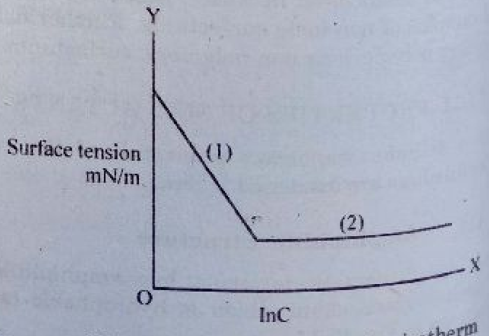


Fig. 11.14: Gibb's adsorption isotherm

11.12 GIBBS'S ADSORPTION EQUATION

"Relationship between the amount of surfactant adsorbed on interface and concentration of surfactant in solution at constant temperature is called Gibb's Adsorption isotherm"

Plot between surface tension and lnC as shown in Fig. 11.14 has two regions. In region (1), surface tension decreases with the increase in value of lnC. This region is called adsorption region or premiceller region and in region (2), surface tension remains constant with change of lnC, this region is called miceller region because micelle formation occurs in this region. Gibb investigated the change of surface tension of liquid with increase of surfactant concentration at constant temperature and formulated it in the form of an equation which is known as Gibb's adsorption isotherm. Mathematically it can be written as

$$\Gamma = \frac{-1}{RT}\left[\frac{d\gamma}{d\ln C}\right]_T \qquad (11.27)$$

Where, Γ is surface excess concentration and its units are mole/m^2 and it can be defined as *"no. of moles of surfactant adsorbed per unit area"*.

Where, $\left[\frac{d\gamma}{d\ln c}\right]_T$ is called the surface activity of surfactant at constant temperature.

Since, $\frac{d\ln C}{dC} = \frac{1}{C}$

So, $d\ln C = \frac{dC}{C}$

By putting value of $d\ln C$ in equation (11.27), we get

$$\Gamma = \frac{-C}{RT}\left[\frac{d\gamma}{dC}\right]_T \qquad (11.28)$$

$$\Gamma = \frac{-C}{2.303RT}\left[\frac{d\gamma}{d\log C}\right]_T \qquad (11.29)$$

$\left[\frac{d\gamma}{d\ln C}\right]_T$ is the ability of surfactant molecules to reduce the interfacial tension between two liquids.

Significance of Gibb's Adsorption Equation

(1) This equation is used to study the adsorption on the surface of a liquid of a substance that dissolves in it.

When $d\gamma/dC$ is positive, i.e. when the surface tension of the solution increases with concentration, Γ must be negative, and the body of solution is richer in solute than the surface, as in the case with many electrolytes and these substances are called surface inactive agents.

However when the surface tension of the solution decreases with concentration, i.e. dγ/dC is negative, Γ is positive and the surface contains higher concentration of solute than the solution. The latter is the case with surface active agents. Positive surface activity is therefore is associated with the adsorption of solute from the solution by the surface of solution, while negative surface activity is due to the expulsion of solute from the surface.

The limiting value of the reduction in surface tension with concentration, i.e.,

$$-\left(\frac{d\gamma}{dC}\right)_{C\to 0}$$ is called surface activity of a substance.

(2) Gibb's equation can also be used to find out the adsorption of gas (vapours) on the surface of a liquid in which it is not soluble, by knowing the variation of γ with P of the adsorbate.

$$d\mu = RT\,d\ln P$$

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d\ln P} = -\frac{P}{RT}\frac{d\gamma}{dP}$$

or

$$\Gamma = -\frac{1}{RT}\frac{\partial\gamma}{\partial\ln P} = -\frac{P}{RT}\frac{\partial\gamma}{\partial P}$$

(3) Area occupied by one molecule of adsorbate (a) can be found by using following equation

$$a = \frac{1}{N_A\Gamma}$$

Gibb's Adsorption Law

It was shown theoretically by Gibbs's that those substances which lower the surface tension of a solvent in which they are dissolve become concentrated in the surface layer, while the concentration of the substances which raise the surface tension is less in the surface layer than in the bulk of the solution.

$$-S = \frac{C}{RT}\frac{d\gamma}{dC}$$

$$S = -\frac{C}{RT}\frac{d\gamma}{dC}$$

Example 11.1

The slope of plot of surface tension vs. natural logarithm of surfactant was found to be -70N/m. Calculate the surface excess concentration at 25 °C in mol/m².

Solution

According to equation (11.27)

$$\Gamma = \frac{-1}{RT}\left[\frac{d\gamma}{d\ln C}\right]_T$$

Where, $\left[\frac{d\gamma}{d\ln C}\right]_{T}$ is the slope of the plot of surface tension vs. natural logarithm of the concentration of surfactant at a constant temperature T and is equal to $-70 Nm^{-1}$ at 298K as given in the question. Hence surface excess concentration will be

$$\Gamma = \frac{70 Nm^{-1}}{\left(8.3143 Jmol^{-1}K^{-1}\right)\left(298K\right)}$$

$$\Gamma = \frac{0.0283 Nm^{-1}}{Nmmol^{-1}} = 0.0283 molm^{-2}$$

11.13 CRITICAL MICELLE CONCENTRATION

Micelle formation occurs due to association of surfactant molecules into bulk phase. *"Single surfactant molecule is called unimer"* and by the combination of unimers micelle formation occurs. *"The number of surfactant molecules present in a micelle is called aggregation number"*. If the micelle is in spherical form, then its radius is called hydrodynamic radius.

Micelles are formed at a certain concentration of surfactant and *"this minimum concentration at which process of micellization starts is called critical micelle concentration (CMC)"*. Below CMC micellization does not occur. Spherical micelle has two regions, hydrophilic region which is called corona and hydrophobic region which is called core as shown in Fig. 11.15. If the concentration of surfactant is less than the critical micelle concentration then it does not stabilize the emulsion.

The value of CMC of a surfactant depends upon temperature, hydrophilic-lipohilic balance (HLB) of surfactant and nature of solvent.

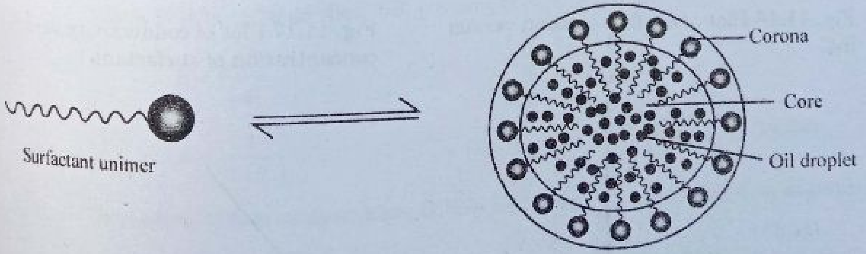


Fig. 11.15 Illustration of micellization and micelle structure

Determination of CMC of a Surfactant

Different methods for the determination of CMC are discussed below

(1) Surface Tension Measurement

Solutions of different concentration of surfactant are prepared and the surface tension of each solution is measured and a graph is plotted between surface tension versus natural logarithm of concentration of surfactant as shown in Fig.

11.16. At initial stages surface tension will decrease with the increase in lnC but after a certain concentration, value of surface tension will become constant. The concentration at which the surface tension of solution becomes constant is called CMC. Because at this concentration micelle formation starts. This method is applicable generally for the determination of CMC of nonionic surfactants.

(2) Conductivity Measurements

Solutions of different surfactant concentrations are prepared and the conductivity of solutions is measured. A graph is plotted between conductivity versus concentration as shown in Fig. 11.17. At initial stage, conductivity and concentration are linear to each other. At certain concentration, conductivity versus conc. plot gives a break. This break will give the value of CMC. Conductivity depends upon the mobility of unimers. After CMC unimers combine and form micelle. Because the mobility of micelle is less than that of unimer so, slope of plot changes at CMC.

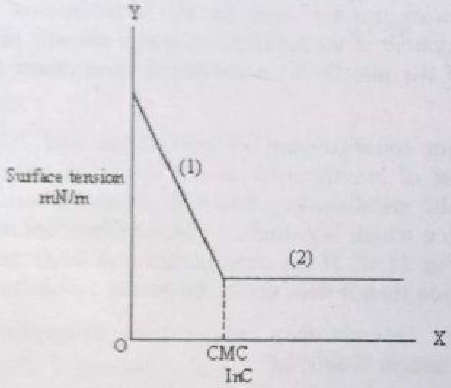


Fig. 11.16 Plot of surface tension versus lnC

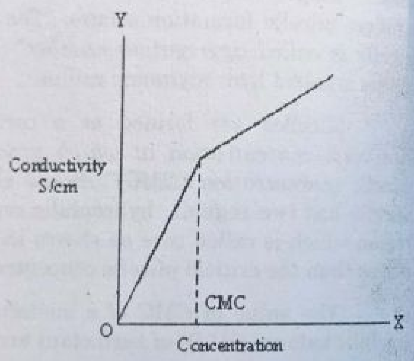


Fig. 11.17 Plot of conductivity versus concentration of surfactant

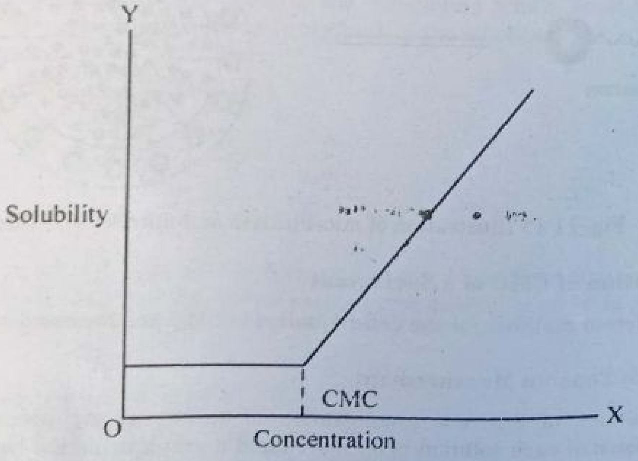


Fig. 11.18 Plot of solubility versus concentration of surfactant

(3) Solubility Measurements

A substance is taken that is insoluble in water. Solutions of different concentrations of surfactant are prepared and the substance that is insoluble in water is added. At lower concentration of surfactant the substance is not soluble because surfactant is present at interface only. But when concentration of surfactant approaches the CMC and surfactant molecules goes in to the bulk then they can solubilize the substance. As a result of which solubility of the substance increases rapidly. Break point of plot of solubility of the substance as function of concentration of surfactant gives the value of CMC of surfactant as shown in Fig. 11.18.

11.14 MICELLIZATION OF NON-IONIC SURFACTANT

Micellization is a reversible process. Initially the rate of formation of micelle is greater than the rate of formation of unimer. A stage at which rate of both processes becomes equal is called dynamic equilibrium. The value of the concentration of the surfactant at the stage of dynamic equilibrium between unimer and micelle is called CMC. Dynamic equilibrium between unimer and micelle of surfactant A can be shown as

$$NA \rightleftharpoons A_N$$

Dividing by N, we get

$$A \rightleftharpoons \frac{1}{N} A_N$$

The equilibrium constant can be written as

$$K = \frac{[A_N]^{1/N}}{[A]}$$

When N is very large then 1/N = 0 and [A]→CMC then,

$$K = \frac{[A_N]^0}{[A]}$$

$$K = \frac{1}{[CMC]} \qquad (11.30)$$

According to thermodynamics, Gibb's free energy for micellization is given by

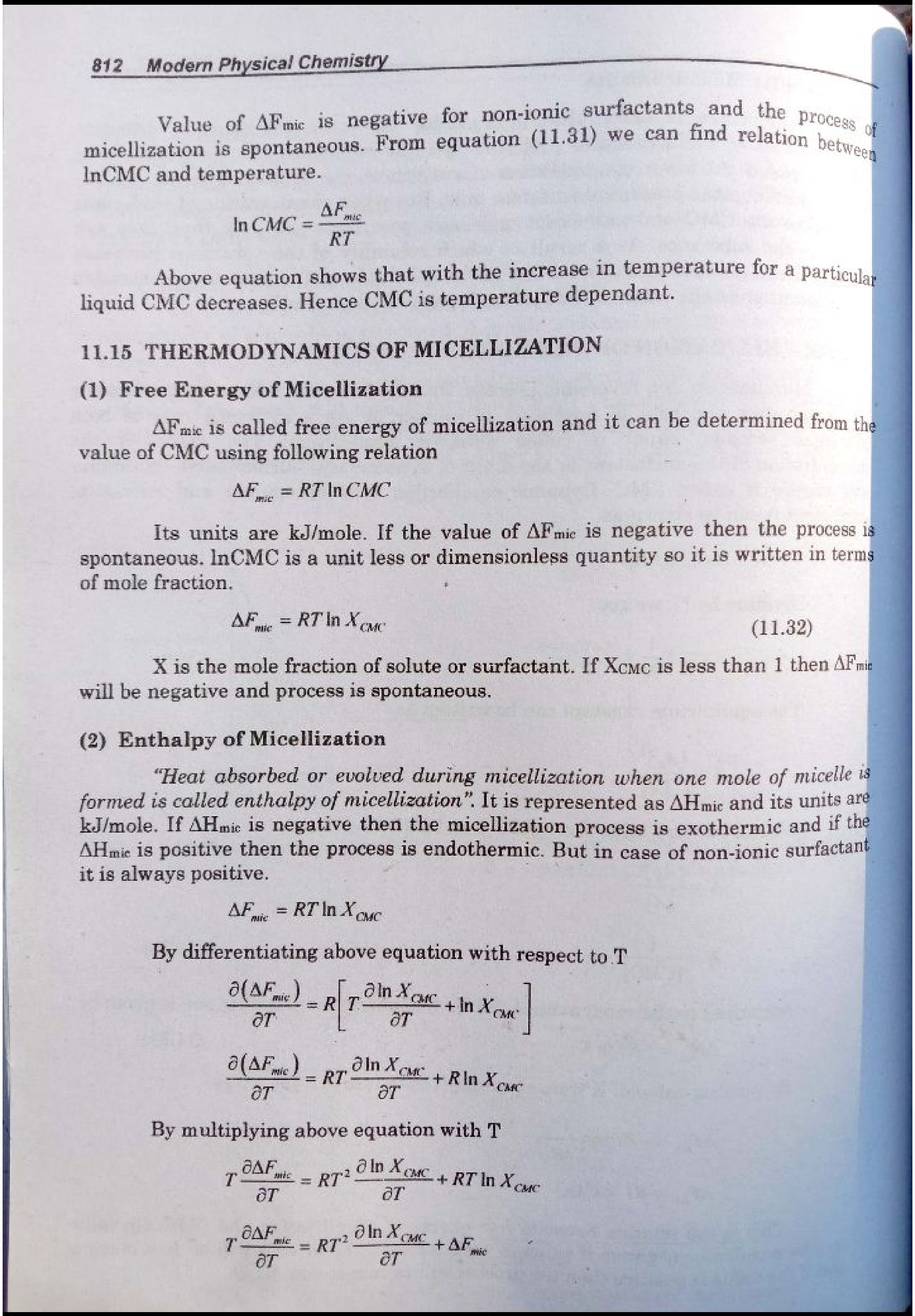
$$\Delta F_{mic} = -RT \ln K \qquad (11.31)$$

By putting value of K from equation (11.30) into (11.31), we get

$$\Delta F_{mic} = -RT \ln \frac{1}{CMC}$$

$$\Delta F_{mic} = RT \ln CMC$$

This is the relation between free energy of micellization and CMC. Its value may be positive or negative if value is negative then the process will be spontaneous and if the value is positive then the process will be non-spontaneous.



Value of ΔF_{mic} is negative for non-ionic surfactants and the process of micellization is spontaneous. From equation (11.31) we can find relation between lnCMC and temperature.

$$\ln CMC = \frac{\Delta F_{mic}}{RT}$$

Above equation shows that with the increase in temperature for a particular liquid CMC decreases. Hence CMC is temperature dependant.

11.15 THERMODYNAMICS OF MICELLIZATION

(1) Free Energy of Micellization

ΔF_{mic} is called free energy of micellization and it can be determined from the value of CMC using following relation

$$\Delta F_{mic} = RT \ln CMC$$

Its units are kJ/mole. If the value of ΔF_{mic} is negative then the process is spontaneous. lnCMC is a unit less or dimensionless quantity so it is written in terms of mole fraction.

$$\Delta F_{mic} = RT \ln X_{CMC} \tag{11.32}$$

X is the mole fraction of solute or surfactant. If X_{CMC} is less than 1 then ΔF_{mic} will be negative and process is spontaneous.

(2) Enthalpy of Micellization

"Heat absorbed or evolved during micellization when one mole of micelle is formed is called enthalpy of micellization". It is represented as ΔH_{mic} and its units are kJ/mole. If ΔH_{mic} is negative then the micellization process is exothermic and if the ΔH_{mic} is positive then the process is endothermic. But in case of non-ionic surfactant it is always positive.

$$\Delta F_{mic} = RT \ln X_{CMC}$$

By differentiating above equation with respect to T

$$\frac{\partial(\Delta F_{mic})}{\partial T} = R\left[T\frac{\partial \ln X_{CMC}}{\partial T} + \ln X_{CMC}\right]$$

$$\frac{\partial(\Delta F_{mic})}{\partial T} = RT\frac{\partial \ln X_{CMC}}{\partial T} + R\ln X_{CMC}$$

By multiplying above equation with T

$$T\frac{\partial \Delta F_{mic}}{\partial T} = RT^2\frac{\partial \ln X_{CMC}}{\partial T} + RT\ln X_{CMC}$$

$$T\frac{\partial \Delta F_{mic}}{\partial T} = RT^2\frac{\partial \ln X_{CMC}}{\partial T} + \Delta F_{mic}$$

$$\Delta F_{mic} - T\frac{\partial \Delta F_{mic}}{\partial T} = -RT^2 \frac{\partial \ln X_{CMC}}{\partial T} \quad (11.33)$$

According to Helmholtz equation

$$\Delta F_{mic} - T\frac{\partial \Delta F}{\partial T} = \Delta H_{mic} \quad (11.34)$$

By comparing equation (11.33) and (11.34), we get

$$\Delta H_{mic} = -RT^2 \frac{\partial \ln X_{CMC}}{\partial T}$$

$$\frac{\Delta H_{mic}}{RT^2}\partial T = \partial \ln X_{CMC}$$

By integrating above equation, we get

$$-\frac{\Delta H_{mic}}{R}\int \frac{1}{T^2}\partial T = \int \partial \ln X_{CMC}$$

$$\ln X_{CMC} = \frac{\Delta H_{mic}}{R}\left(\frac{1}{T}\right) + c \quad (11.35)$$

This is an equation of straight line with intercept form as shown in Fig. 11.19.

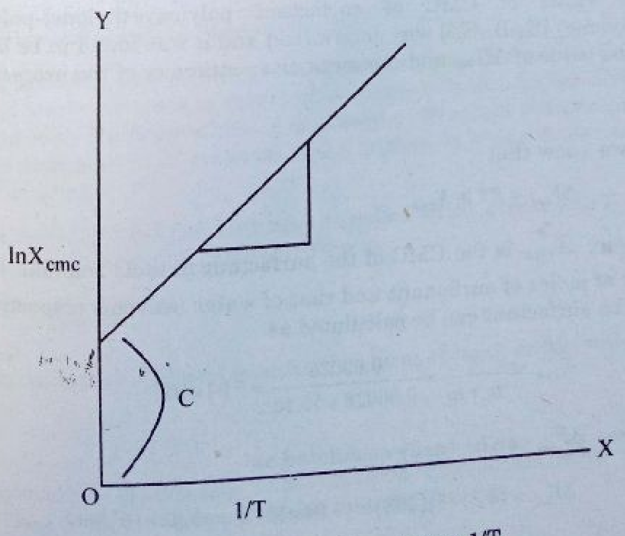


Fig. 11.19 Plot of lnX$_{CMC}$ versus 1/T

ΔH_{mic} can be determined from the slope as

$$\text{slope} = \frac{\Delta H_{mic}}{R}$$

$$\Delta H_{mic} = \text{slope} \times R$$

Slope is positive which shows that ΔH_{mic} is positive which indicates that process is endothermic.

(3) Entropy of Micellization

It is represented by ΔS_{mic} and its units are $JK^{-1}mole^{-1}$. Entropy of micellization is zero or positive for spontaneous process (according to 2nd law of Thermodynamics). When surfactant diffuse into the bulk, then it breaks the structure of water and creates disorderness among the water molecules, hence entropy is increased. When micelle is formed, then due to hydrophobic core water is expelled to the surrounding due to hydrophobic core, hence entropy increased. Both these factors are the causes behind increase in entropy of the system. Entropy of micellization can be calculated using fundamental relation of thermodynamics as

$$\Delta F_{mic} = \Delta H_{mic} - T\Delta S_{mic}$$

$$\Delta S_{mic} = \frac{\Delta H_{mic} - \Delta F_{mic}}{T} \qquad (11.36)$$

Example 11.2

The value of CMC of surfactant poly(oxyethylene)-poly(oxybutylene)-poly(oxyethylene) [$E_{20}B_{10}E_{20}$] was determined and it was found to be 0.56g/L at 25°C. Calculate the value of ΔG_{mic} and comment on spontaneity of the process.

Solution

As we know that

$$\Delta F_{mic} = RT \ln X_{CMC}$$

Where, X_{CMC} is the CMC of the surfactant in mole fraction. If n_1 and n_2 are the number of moles of surfactant and that of water (solvent) respectively, then mole fraction of the surfactant can be calculated as

$$X_{CMC} = \frac{n_1}{n_1 + n_2} = \frac{0.00028}{0.00028 + 55.56} = 5.04 \times 10^{-6}$$

Hence ΔF_{mic} can be easily calculated as

$$\Delta F_{mic} = (8.3143)(298)\ln\left(5.04 \times 10^{-6}\right) = -3.02 \times 10^{4}\ \text{Jmol}^{-1}$$

11.16 TECHNIQUES USED TO STUDY MICELLIZATION PARAMETERS

(1) Surface Tensiometry

Surface tension measurement can be used for the determination of CMC, critical surface tension γ_{cmc} (surface tension at CMC), surface pressure, free energy of micellization, enthalpy of micellization and entropy of micellization. Fig. 11.20 gives plot of surface tension as a function of natural logarithem of concentration of surfactant. The value of CMC can be determined from the plot. The value of critical surface tension corresponds to CMC can be measured from the plot in Fig. 11.20. The difference between surface tension of pure water and surfactant containing water at various concentration gives value of surface pressure ($\pi = \gamma_0 - \gamma_{cmc}$). Free energy of micellization, enthalpy of micellization and entropy of micellization can be determined using equations (11.11), (11.14) and (11.15) respectively.

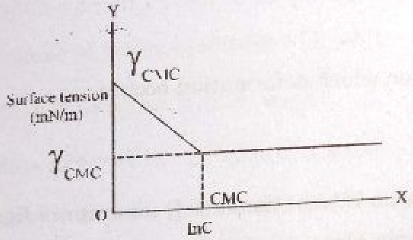


Fig. 11.20 Plot of surface tension versus lnC

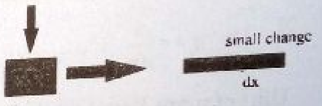


Fig. 11.21 Deformation of material

(2) Viscosity and Density Measurements

The viscosity and density measurements give information about elasticity of micelles and water contents in core and corona region of micelles. The term viscosity is associated with rheology which is a science of flow and deformation of materials.

The deformation of material is the change in shape under external force as shown in Fig. 11.21.

The force applied per unit area is called shear stress and its unit are Nm^{-2}. Mathematically shear stress can be written as

$$\tau = \frac{F}{A}$$

The change in length is measured in term of shear strain which is

$$\gamma = \frac{\Delta X}{X}$$

According to Hook's Law of deformation of materials, shear stress and shear strain are directly related to each other i.e.

$$\tau \propto \gamma$$

$$\tau = G\gamma$$

Where proportionality constant G is called Young's modulus. The rate of change of strain with respect to time is called shear rate and its unit are s^{-1} and mathematically can be written as

$$\text{Shear rate} = \gamma^{o} = \frac{d\gamma}{dt}$$

Newton gave a relation between shear stress and shear rate to define the viscosity and this relation is called Newton law of viscosity which is given below

$$\tau \propto \gamma^{o}$$

$$\tau \propto \frac{d\gamma}{dt}$$

$$\tau = \eta \frac{d\gamma}{dt}$$

Where η is viscosity of material on which deformation occurs

$$\eta = \tau \frac{dt}{d\gamma}$$

Unit of η are Nsm^{-2} while in System International (S.I) its unit are $Kgm^{-1}s^{-1}$.

τ represents absolute or dynamic viscosity. If material has the ability to follow the Newton law of viscosity is called the Newtonian material otherwise Non-Newtonian material.

Relative viscosity (η_{rel}) and specific viscosity (η_{sp}) are unitless quantities and represented by following equations.

$$\eta_{rel} = \frac{\eta_{solution}}{\eta_{solvent}}$$

$$\eta_{sp} = \eta_{rel} - 1$$

Reduced viscosity (η_{red}) is the ratio of specific viscosity to the concentration of surfactant and is represented by

$$\eta_{red} = \frac{\eta_{sp}}{c}$$

By plotting a graph between concentration and reduced viscosity as shown in Fig. 11.22. The intrinsic viscosity [η] can be determined and defined as *"the value of reduced viscosity when concentration approaches to zero"*.

[η] can be used to estimate the quantity of water inside the micelle. We can derive an expression for water contents inside the micelle and intrinsic viscosity. Water contents are decreased by increasing the temperature of the system, size of micelle also decreases as shown in Fig. 11.22.

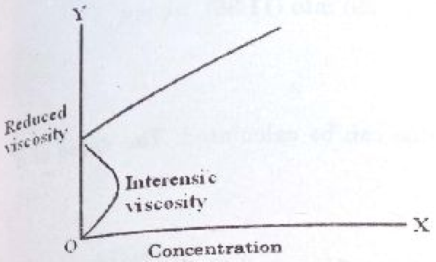


Fig. 11.22 Plot of reduced viscosity versus concentration

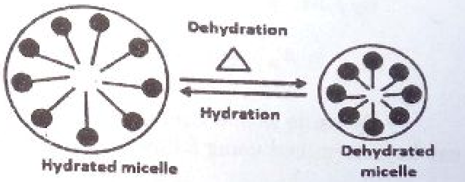


Fig. 11.23 Decrease in size of micelle due to expulsion of water

Volume of hydrated micelle = V_h

Volume of anhydrous micelle = V_a

Volume of water in micelle $= (V_h - V_a)$

Mass of water in micelle $= \rho_o (V_h - V_a)$

Mass of water in one mole of micelle $= \rho_o N_A (V_h - V_a)$

1 g of water in 1 g of micelle is called hydration value. So,

$$\text{Hydration value} = \frac{\rho_o N_A (V_h - V_a)}{\text{Molar mass of micelle}}$$

$$\text{Hydration value} = \frac{\rho_o N_A (V_h - V_a)}{M_{mic}}$$

$$W_h = \frac{\rho_o N_A V_a}{M_{mic}} \left(\frac{V_h}{V_a} - 1 \right) \tag{11.37}$$

Where, u' is called partial specific volume and is determined by following relation

$$\upsilon' = \frac{N_A V_a}{M_{mic}}$$

By replacing $N_A V_a / M_{mic}$ with u' in equation (11.37), we get

$$W_h = \upsilon' \rho_o \left(\frac{V_h}{V_a} - 1 \right) \tag{11.38}$$

Einstein gave a relation among intrinsic viscosity, partial specific volume and, volume of hydrated and anhydrated micelle by considering micelles as sphere suspended in liquid i.e.

$$\frac{[\eta]}{2.5\upsilon'} = \frac{V_h}{V_a} \tag{11.39}$$

By putting value of V_h/V_a from equation (11.39) into (11.38), we get

$$W_h = \upsilon\rho_o\left(\frac{[\eta]}{2.5\upsilon'} - 1\right)$$

By using above equation hydration value can be calculated. The value of u' can be determined using following equation

$$\rho = (1-\upsilon'\rho_o)C + \rho_o$$

This is an equation of straight line in intercept form whose intercept is ρ_o and slope is $1-\upsilon'\rho_o$. And $\frac{[\eta]}{\upsilon'}$ is the shape factor of micelle which is equal to u.

If micelle is rigid, anhydrous and spherical then $\nu = \frac{[\eta]}{\nu'} = 2.5$

Hence, viscosity and density measurements give information about elasticity of micelles, water contents in a micelle and shape of micelles.

(1) Dynamic Light Scattering (DLS)

Dynamic light scattering is used to determine the size of micelles, size distribution of micelles and variation in size of micelles with change in temperature.

Light scattering is of two types.

(a) Rayleigh Scattering

When size of a particle is smaller than wavelength of radiation, then Rayleigh scattering occurs. Wavelength of incident and scattered radiation remains same in it. This is elastic scattering. If particle size is larger, then scattered radiations reach the detector with phase difference and result in interference effect.

(b) Raman Scattering

It is inelastic scattering and is exhibited by relatively larger particles. Here, wavelength of scattered radiation is not equal to that of incident one, so if energy is absorbed by molecule then scattered photons will be of lower frequency and if photons gain energy from molecule then scattered radiation will be of higher frequency. Fig. 11.24 depicts the scattering of light in miceller solution.

The magnitude of scattering vector (q) can be written as

$$q = \frac{4\pi n}{\lambda}\left(\sin\frac{\theta}{2}\right)$$

Where α is the wavelength of light, θ is scattering angle and n is refractive index of solvent. Fig. 11.25 shows plot of intensity of scattering light as a function of time.

$$\Gamma = \frac{1}{\tau}$$

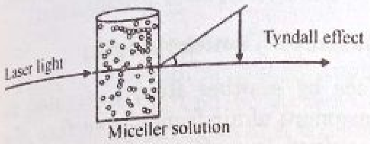


Fig. 11.24 Scattering of light

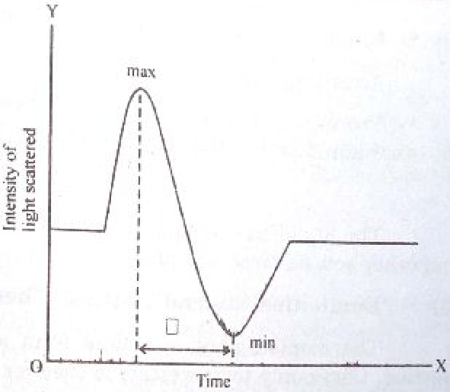


Fig. 11.25 Intensity of scattered light as a function of time

Γ is the decay rate and τ is the delayed period which is the difference between the maximum and minimum value of scattering intensities. Maximum scattering occurs when particle is in the path of light and scattering decreases when particles move away from light path. Decay rate is related to scattering vector as

$$\Gamma = Dq^2$$

Where D is the diffusion co-efficient and q is scattering vector.

According to Stokes-Einstein equation diffusion coefficient is given by

$$D = \frac{k_B T}{6\eta\pi R_h} \qquad (11.40)$$

Where, k_B is Boltzmann constant, R_h is the hydrodynamic radius of micelle, T is absolute temperature and η is the viscosity of solvent. Equation (11.40) gives the value of hydrodynamic radius.

11.17 THEORIES OF EMULSION TYPE

Theories of emulsion type fall into two categories

(1) Qualitative Theories

(2) Quantitative Theories

11.17.1 Qualitative Theories

(1) **Theory of Interfacial Tension**

According to this theory, the interfacial tension between oil and surfactant and that between water and surfactant determines the type of emulsion. If the surface tension between water and surfactant is greater than that between oil and surfactant i.e.; $\gamma_{ws} > \gamma_{os}$, then water in oil emulsion is formed and vice versa.

(2) Banscroft's Rule of Emulsion Type

According to Bancroft's rule

The liquid in which emulsifier is more soluble acts as a continuous phase and the other liquid acts as discontinuous phase

or

The liquid having more ability to wet the emulsifier acts as continuous phase and other acts as dispersed phase.

(3) Emulsification and Wetting (Theory Based on Contact Angle)

The displacement of a fluid from a surface by another fluid is termed as wetting. Commonly term wetting is used for displacement of air from the surface of a solid by a liquid. Three immiscible phases are involved in wetting process. Out of these three phases, at least two phases are fluids. Wetting ability of a fluid is measured in terms of contact angle as shown in Fig. 11.26. When the contact angle of droplet of liquid with the solid surface is low, its wetting ability is high whereas a large contact angle corresponds to low wetting ability.

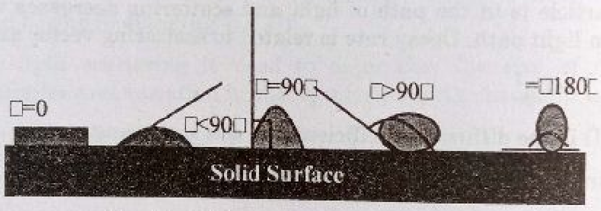


Fig. 11.26 Contact angle and wetting

Measurement of Contact Angle

When a drop is static, then the sum of all the forces along x-axis becomes zero.

According to Young's equation,

$$\gamma_{vs} = \gamma_{sl} + \gamma_{lv}\cos\theta \qquad (11.41)$$

Where, $\gamma_{vs}, \gamma_{sl}, \gamma_{lv}$, is the interfacial tension between vapor and solid, solid and liquid and liquid and vapor respectively. While, θ is the contact angle between solid and liquid as shown in Fig. 11.27.

If the values of the interfacial tensions are known then we can determine the value of contact angle. From equation (11.41), we get

$$\cos\theta = \frac{\gamma_{vs} - \gamma_{sl}}{\gamma_{lv}} \qquad (11.42)$$

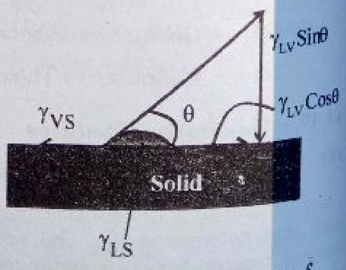


Fig. 11.27 Measurement of contact angle

According to equation (11.42) when we add surfactant into a liquid, it decreases its surface tension (γ_{lv}) and increases value of cosθ but decreases value of contact angle. In other words, surfactant increases the wetting ability of a liquid by lowering its surface tension. Such chemical substances are called wetting agents. The liquid having high wetting ability will serve as continuous phase in emulsion. If the angle of contact of the droplet with emulsifier is less than 90° then the liquid will act as a dispersed phase and vice versa.

Orientation Wedge Theory

In orientation theory, the type of emulsion depends upon the cross sectional area of hydrophillic and hydrophobic end of the surfactant. If the cross sectional area of hydrophilic end of surfactant is larger than hydrophobic end then surfactant adopts configuration in a micelle in such a way that hydrophobic portion will remain outward to form o/w emulsion as shown in Fig. 11.28 (a). If cross sectional area of hydrophobic group is greater than that of hydrophilic portion then hydrophobic side of surfactant will be directed outward to give w/o emulsion as shown in Fig. 11.28 (b).

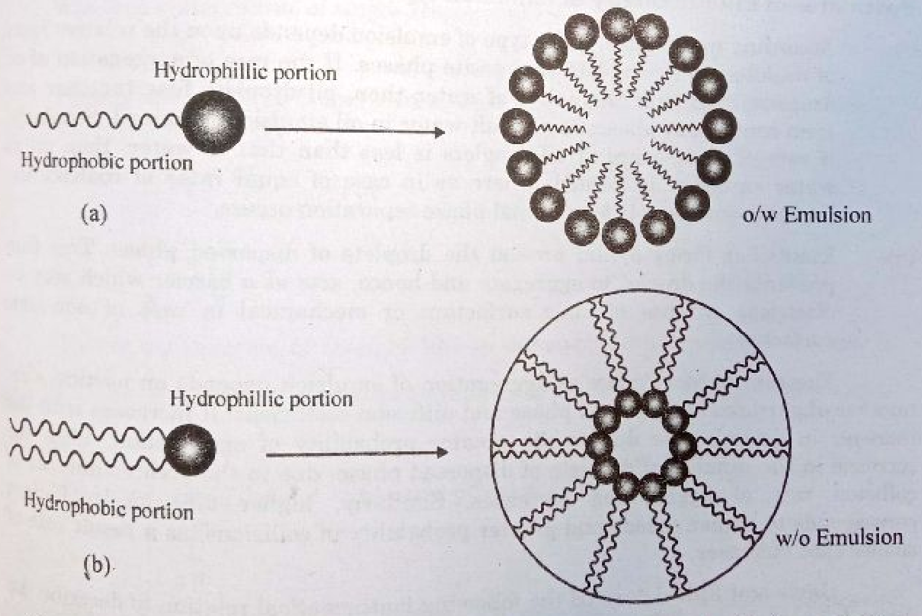
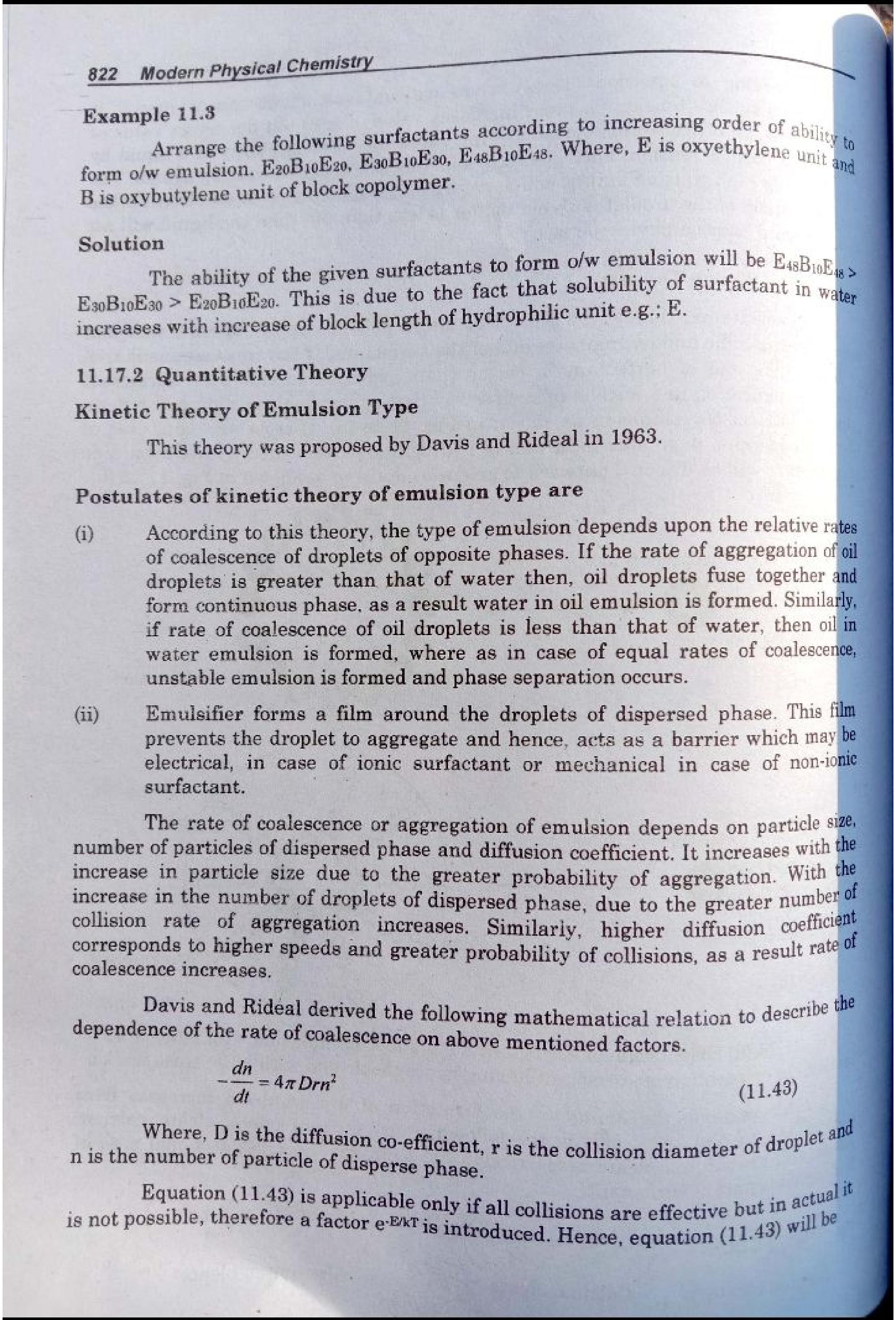


Fig. 11.28 (a) Orientation of surfactant having hydrophillic end with large cross section, (b) orientation of surfactant having hydrophobic end with large cross section

For example the ability of the formation of w/o emulsion increases from sodium salt to aluminum salt in the following surfactants (sodium oleate, calcium oleate and aluminium oleate respectively) due to inverse in cross sectional area of hydrophobic part of surfactant.

$H_3C{+}(CH_2)_{16}{+}COONa$ $\left(H_3C{+}(CH_2)_{16}{+}COO^-\right)_2 Ca^{2+}$ $\left(H_3C{+}(CH_2)_{16}{+}COO^-\right)_3 Al^{3+}$

Sodium oleate Calcium oleate Aluminium oleate



Example 11.3

Arrange the following surfactants according to increasing order of ability to form o/w emulsion. $E_{20}B_{10}E_{20}$, $E_{30}B_{10}E_{30}$, $E_{48}B_{10}E_{48}$. Where, E is oxyethylene unit and B is oxybutylene unit of block copolymer.

Solution

The ability of the given surfactants to form o/w emulsion will be $E_{48}B_{10}E_{48} > E_{30}B_{10}E_{30} > E_{20}B_{10}E_{20}$. This is due to the fact that solubility of surfactant in water increases with increase of block length of hydrophilic unit e.g.; E.

11.17.2 Quantitative Theory

Kinetic Theory of Emulsion Type

This theory was proposed by Davis and Rideal in 1963.

Postulates of kinetic theory of emulsion type are

(i) According to this theory, the type of emulsion depends upon the relative rates of coalescence of droplets of opposite phases. If the rate of aggregation of oil droplets is greater than that of water then, oil droplets fuse together and form continuous phase, as a result water in oil emulsion is formed. Similarly, if rate of coalescence of oil droplets is less than that of water, then oil in water emulsion is formed, where as in case of equal rates of coalescence, unstable emulsion is formed and phase separation occurs.

(ii) Emulsifier forms a film around the droplets of dispersed phase. This film prevents the droplet to aggregate and hence, acts as a barrier which may be electrical, in case of ionic surfactant or mechanical in case of non-ionic surfactant.

The rate of coalescence or aggregation of emulsion depends on particle size, number of particles of dispersed phase and diffusion coefficient. It increases with the increase in particle size due to the greater probability of aggregation. With the increase in the number of droplets of dispersed phase, due to the greater number of collision rate of aggregation increases. Similarly, higher diffusion coefficient corresponds to higher speeds and greater probability of collisions, as a result rate of coalescence increases.

Davis and Rideal derived the following mathematical relation to describe the dependence of the rate of coalescence on above mentioned factors.

$$-\frac{dn}{dt} = 4\pi Drn^2 \tag{11.43}$$

Where, D is the diffusion co-efficient, r is the collision diameter of droplet and n is the number of particle of disperse phase.

Equation (11.43) is applicable only if all collisions are effective but in actual it is not possible, therefore a factor $e^{-E/kT}$ is introduced. Hence, equation (11.43) will be

$$-\frac{dn}{dt} = 4\pi Drn^2 e^{-\frac{E}{kT}} \tag{11.44}$$

Separating the variables and integrating equation (11.44), we get

$$-\int \frac{dn}{n^2} = 4\pi Dre^{-\frac{E}{kT}} \int dt$$

$$\frac{1}{n} = 4\pi Dre^{-\frac{E}{kT}} t + c \tag{11.45}$$

This is an equation of straight line in intercept form with slope $4\pi Dre^{-\frac{E}{kT}}$.

According to Stoke- Einstein equation we know

$$D = \frac{kT}{6\pi\eta a} \tag{11.46}$$

Where, a is the radius of single droplet and

$$r = 2a \tag{11.47}$$

Putting the value of D and r from equation (11.46) and (11.47) respectively into equation (11.45), we get

$$\frac{1}{n} = 4\pi \frac{kT}{6\pi\eta a} 2ae^{-\frac{E}{kT}} t + c$$

$$\frac{1}{n} = \frac{4}{3}\frac{kT}{\eta} e^{-\frac{E}{kT}} t + c \tag{11.48}$$

This is an equation of straight line in intercept form, the slope of which is equal to $\frac{4}{3}\frac{kT}{\eta} e^{-\frac{E}{kT}}$. Hence, E can be calculated from the slope if all other parameters are known.

Mean volume of droplet of disperse phase is given as below

$$\overline{V} = \frac{V}{n} \tag{11.49}$$

Where V is the total volume of the disperse phase and n is the number of droplets of dispersed phase.

Putting the value of 1/n from equation (11.48) into equation (11.48), we get

$$\overline{V} = V\left[\frac{4}{3}\frac{kT}{\eta} e^{-\frac{E}{kT}} t + c\right]$$

$$\overline{V} = \frac{4}{3}\frac{VkT}{\eta} e^{-\frac{E}{kT}} t + cV$$

11.19 BREAKING OF EMULSION (DEMULSIFICATION)

The process of separating the two constituent liquids of emulsion into tw layers is called the breaking of emulsion. It is due to the aggregation of the droplet of the dispersed phase and may occur in the form of creaming, sedimentation o coalescence as shown in Fig. 11.30.

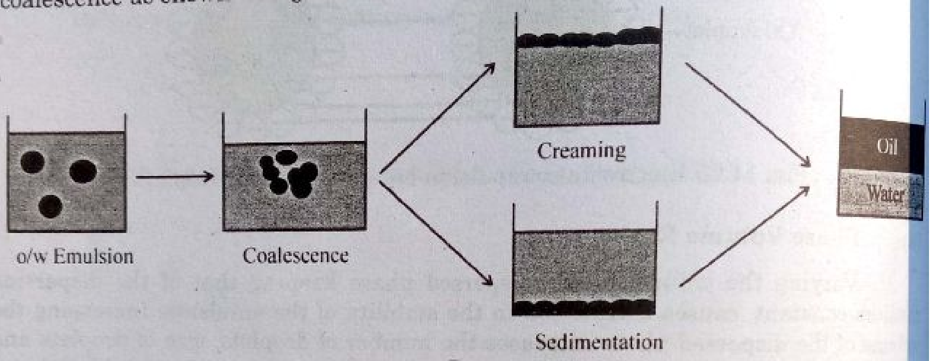


Fig. 11.30 Emulsion breaking by coalescence

Coalescence

When droplets of the dispersed phase aggregate to form a single larger drop, this phenomenon is called as coalescence or coagulation. This coagulation ultimately leads to phase separation. Creaming and sedimentation are two types of coagulation depending upon position of dispersed phase. When the droplets of dispersed phase collect on the surface of emulsion due to small density of dispersed phase, this phenomenon is called as creaming. While sedimentation involves aggregation of droplets of dispersed phase at the bottom of the emulsion due to high density of dispersed phase.

Methods of Demulsification

Some of the methods of demulsification are discussed below

(1) Chemical Method

It involves the addition of an electrolyte to the emulsion that causes aggregation by the removal of charge on the emulsifier and demulsify the emulsion. The quantity of the electrolyte needed to cause aggregation depends upon charge on its cation according to the Hardy Schulze rule.

(2) Mechanical Method

Mechanical methods such as centrifugation or ultrafiltration can be used to separate the two phases present in an emulsion.

(3) Electrical Method

Electrophoresis is one of the frequently used electrical methods for breaking the emulsions in which the charged particles of the emulsifier migrate towards the oppositely charged electrodes and get discharged and precipitated.

(4) Physical Method

Demulsification can also be carried out by heating. Increasing the temperature increases the rate of coalescence, causing the emulsion to become less stable and ultimately break it.

11.20 METHODS OF EMULSION PREPARATION

Emulsification

The process of formation of emulsion by mixing two immiscible liquids with each other in the presence of emulsifier is called emulsification. It involves the breaking of the internal phase into droplets by means of mechanical energy and then stabilizing these droplets in continuous phase with the help of emulsifier.

Methods of emulsification include the conventional as well as advanced methods.

(1) Conventional Methods

The conventional methods usually employed are

(a) Laboratory Method

In this method an organic liquid is stirred with water in the presence of emulsifier for certain period of time to produce an emulsion.

(b) Industrial Method

In this method, dispersed phase and continuous phase along with an emulsifier are sprayed from opposite sides. They mix with each other in the centre to form an emulsion as shown in Fig. 11.31.

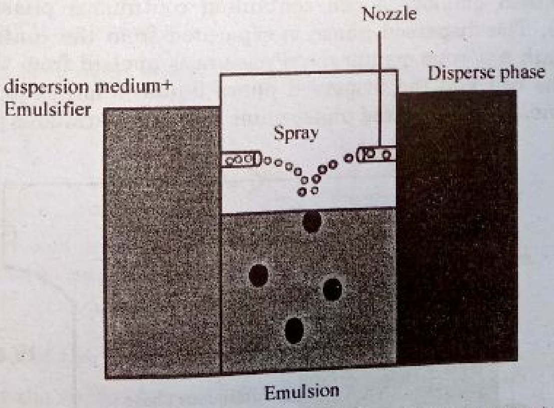


Fig. 11.31 Emulsion preparation on industrial scale by conventional method

(2) Advanced Methods

Membrane emulsification is one of the advanced techniques for preparing emulsions which makes use of a porous membrane. It is further divided into indirect and direct methods.

Indirect Membrane Emulsification Method

In this method, pressure is applied to push the emulsion prepared by classical method through a porous membrane to get a monodisperse emulsion as shown in Fig. 11.32. After passing through the pores of the membrane, the droplets of uniform size are formed.

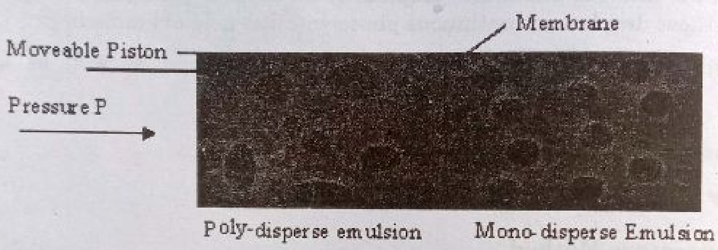


Fig. 11.32 Indirect membrane emulsification method

Direct Method

Direct method includes stirred cell and cross flow methods.

(1) Stirred Cell Method

This method employs a cell containing continuous phase, emulsifier and dispersed phase. The dispersed phase is separated from the continuous phase and emulsifier through a porous membrane. Pressure is applied from the disperse phase liquid side of the cell and the dispersed phase liquid is forced to pass through the porous membrane. Thus dispersed phase enter into the continuous phase where a

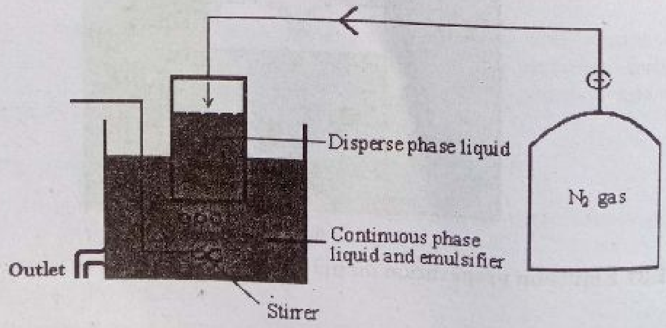


Fig. 11.33 Stirred cell method

stirrer mixes these droplets into the continuous phase in the presence of an emulsifier and the resulting emulsion is passed through an outlet and is collected in a container as shown in Fig. 11.33.

(2) Cross Flow Method

In this method, direction of flow of dispersed phase and continuous phase along with an emulsifier is perpendicular. Thus they mixed with each other perpendicularly to form an emulsion and are collected in separate cells through an outlet as shown in Fig. 11.34. This method employs porous membrane after passing through which small sized droplets of dispersed phase are formed.

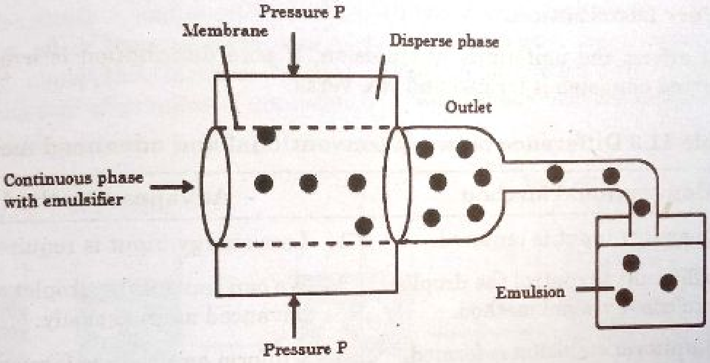


Fig. 11.34 Cross flow method

In this method, the particle size depends on the following factors

(1) Pore Size of Membrane

Particle size is directly related with the pore size of membrane as described by the equation given below

$$\overline{d_d} = \overline{d_p}$$

Where $\overline{d_d}$ and $\overline{d_p}$ represent the average diameter of the droplet and that of the pores of membranes respectively. c is the constant of proportionality. It is a dimensionless quantity and its value depends on the nature of the material of membrane.

(2) Flow Speed of the Continuous Phase

The greater the speed of flow of continuous phase, the smaller will be the size of the particle. Greater speed applies greater force on the droplet to get it released from the membrane pore and small sized droplets are formed.

(3) Pore Density

It is defined as the number of pores per unit area of membrane. High pore density implies that the pores lie very close to each other. Therefore the droplets in the adjacent pores may combine to form larger droplet. A low pore density leads to the formation of small number of droplets. Thus one has to compromise on quantity of droplets to prevent aggregation of droplets.

(4) Pressure

Particle size increases with pressure as high pressure causes greater volume of liquid to come out in lesser period of time.

(5) Pore Distribution

It affects the uniformity of emulsion. If pore distribution is irregular, then polydispersed emulsion is formed and vice versa.

Table 11.3 Difference between conventional and advanced methods

Conventional Method	Advanced Method
1. High energy input is required.	1. Less energy input is required
2. It is difficult to control the droplet size in conventional method.	2. We can control the droplet size in advanced method easily.
3. Non uniform emulsion is formed.	3. Uniform emulsion is formed.
4. The emulsion formed is less stable.	4. More stable emulsion is formed.
5. Droplet size distribution is broad.	5. Droplet size distribution is uniform.
6. Macro level emulsion is produced	6. Micro as well as nano level emulsion can be produced

11.21 APPLICATIONS OF EMULSIONS

(1) Drug Delivery

Drug is hydrophobic in nature and hence not completely soluble in water. The surfactant molecules, after being added, form micelles in the solution and the drug gets entrapped in the core of these micelles. When these micelles enter into the body, they get collapsed at a certain temperature or pH and thus the drug is delivered to the body.

(2) Enhanced Oil Recovery

Three different ways can be employed for oil recovery which include

(i) **Primary oil recovery:** In this method, oil is pumped out of the reservoir through suction pumps. 6 – 15% of the oil is recovered through this method.

(ii) **Secondary oil recovery:** In this method, oil is recovered through flooding. 15 – 30% of the oil is recovered by this method.

(iii) **Tertiary oil recovery:** In this method, oil is recovered through emulsification. An aqueous solution of surfactant is added to the oil reservoir which forms an o/w emulsion. This emulsion is then pumped out through suction pumps. 30 – 60% of oil is recovered by this method.

(3) Emulsions as Microreactors

Emulsions are used as microreactors. For example, when two hydrophilic reactants A and B have been solubilized separately in the presence of a surfactant to give w/o emulsions, the surfactant forms a film around the reactants. If the two emulsions are mixed, then there is an exchange of reactants through collision of water droplets or coagulation of two droplets to form a single droplet as shown in Fig. 11.35. Reactants A and B collide with each other again and again to form product. This cage effect increases the rate of reaction. Recently, metal nanoparticles are prepared using this method. Size of metal nanoparticles can be controlled by controlling size of droplets of emulsion. We can also stabilize metal nanoparticles by this method.

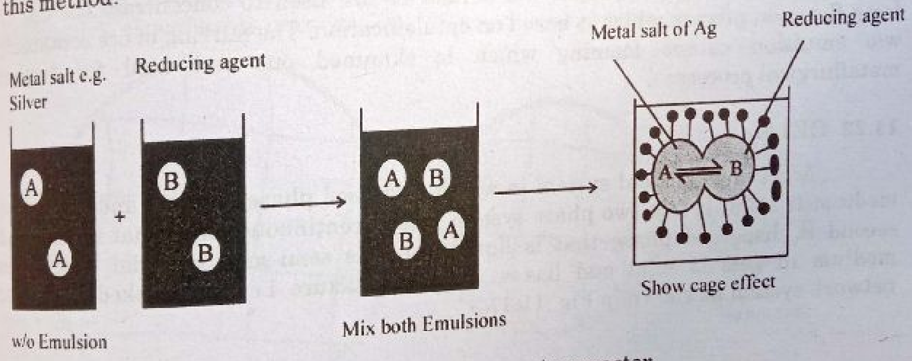


Fig. 11.35 Emulsions as microreactor

(4) Detergents Action

Detergents also work on the principle of emulsification as shown in Fig. 11.36. Surfactant is added to water in order to remove the oil droplets from the cloth, it forms micelles that entrap the oil droplets in hydrophobic core and on the removal of the detergent, oil droplet also gets removed from the surface of the clothes.

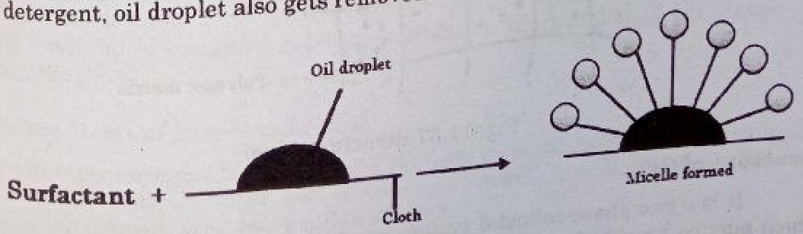


Fig. 11.36 Cleaning action of soap

(5) Food Industry

Food industry also makes use of the process of emulsification. For example, milk is an emulsion which is stabilized by an emulsifier named casein. The food we cook is usually an emulsion containing oil, water and a variety of sausages. Likewise, the process of baking also involves the addition of an emulsifier named as diacetyl tartaric (acid) ester of monoglycerides and abbreviated as DATEM.

(6) Cosmetic Industry

Many different emulsifiers are used in cosmetics to prepare emulsions such as cream or lotion etc. which help them to spread and get absorbed or adsorbed by the skin, because skin also has hydrophillic and hydrophobic dual nature. Common examples of emulsifiers used in cosmetic industry include emulsifying wax, cetyl alcohol, poly sorbate 20 (Tween 20).

(7) Froth Flotation Process

In metallurgical process, w/o emulsions are used to concentrate the ore by froth flotation process which is based on emulsification. The stirring of ore containing w/o emulsion causes foaming which is skimmed out and used for further metallurgical processes.

11.22 GELS

A gel is a colloidal system in which dispersed phase is liquid and dispersion medium is solid. It is a two phase system, one is continuous phase that is solid and second is dispersed phase that is liquid. So it is semi-solid material. Dispersion medium in gels is solid and has a specific structure i.e. cross-linked polymeric network system as shown in Fig. 11.37.

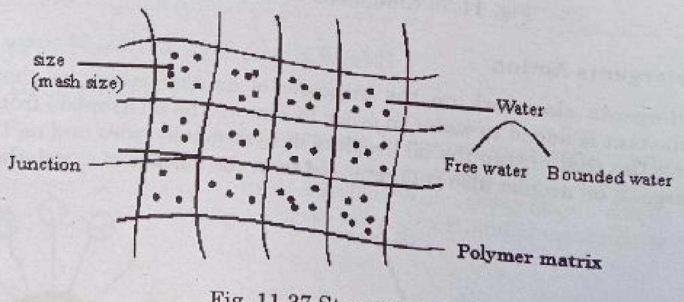


Fig. 11.37 Structure of gel

Structure of Gels

It is a two phase colloidal system in which continuous phase is solid material which may be branched or cross-linked polymer system. While, discontinuous phase is liquid and if this liquid is water it is called hydrogel. In case of hydrogels the water entrapped in the network may be of three types.

(1) **Primary bound water:** Water bound to polymer network through hydrogen bonding.

(2) **Secondary bound water:** Water bound to polymer through hydrophobic interactions (Vander Waal forces). Primary and secondary bound water called total bound water.

(3) **Free water:** Water that can freely enter or leave the network all the time is called free water.

Classification of Gel

On different basis, gels can be classified as listed below

(1) On the Basis of the Size of Polymer Matrix or Dispersion Medium

On the basis of size of polymer matrix, gel is divided into three types as shown in Fig. 11.38. If particle size of gel is very large then gel system is called macro gels. If particle size of gel is in range of 0.1-1 μm, then gel system is called micro gels and if particle size of gel is in range of 1-100 nm then gel system is called nano gels.

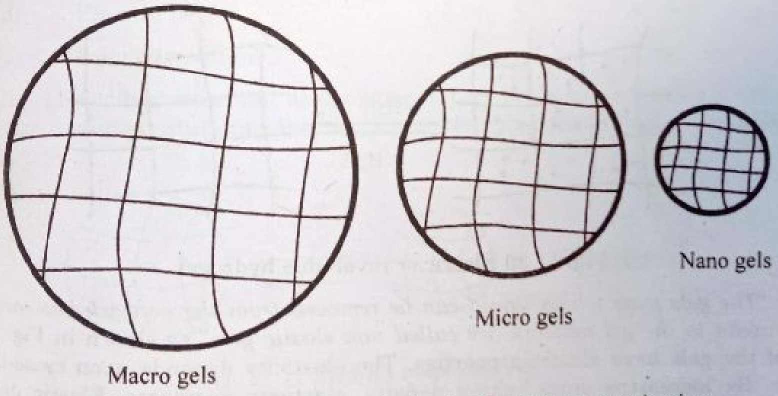


Fig. 11.38 Classification on the basis of polymer matrix size

(2) On the Basis of Nature of Dispersion Medium

If network is made up of organic polymer then gel system is called organo gel and if it is made up of inorganic polymer (silicone or silica etc) then gel system is called inorganic gel.

(3) On the Basis of Disperse Liquid

If water is entrapped in the network then gel is called hydrogel. If benzene is entrapped in the network then gel is called benzogel. Similarly, if alcohol is entrapped in the network then gel is called alcogels.

(4) On the Basis of Nature of Cross-Linkage

On the basis of cross-linkage gels are divided into two types.

(a) Physically cross-linked gels are such gels in which vander waal's forces are present in the network.

(b) Chemically cross-linked gels possess chemical bonding is present in the network.

(5) On the Basis of Physical Properties

On the basis of elasticity, the hydrogels can be classified as

(a) Elastic

(b) Nonelastic

"The gels from which liquid can be removed and can be added again with reversible size variation of gel particle are called elastic gels". These are also known as reversible hydrogels as shown in Fig. 11.39.

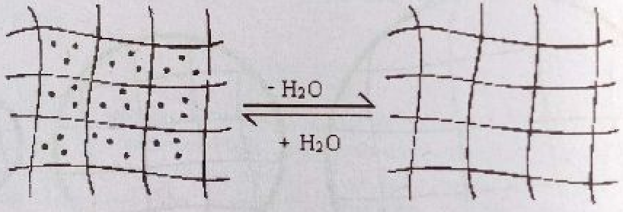


Fig. 11.39 Elastic or reversible hydrogel

"The gels from which liquid can be removed from the network but cannot be added again to the gel network are called non elastic gels" as shown in Fig. 11.40. Most of the gels have elastic properties. The elasticity depends upon cross-linking density. By increasing cross-linking density, elasticity decreases. Elastic gels can swell or shrink with change in conditions like temperature, ionic strength and pH of the medium.

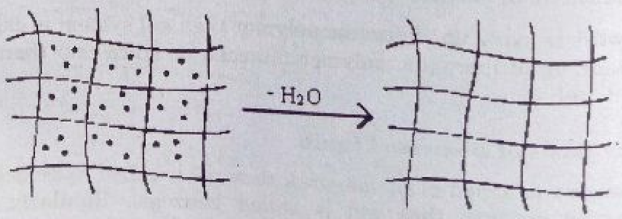


Fig. 11.40 Non elastic gel

(6) On the Basis of Amount of Dispersed Phase (Liquid-Solid Network)

If liquid or dispersed phase in gel is 95% or more then gel is called jelly. If liquid or dispersed phase in gel is less than 95% then gel is called simple gel. Xerogels can be obtained by removal of liquid from the gel network but liquid cannot be removed completely from gels. Aero-gels are obtained by replacing liquid with air.

(7) On the Basis of Responsive Behavior

(a) Responsive Gels

Responsive gels swell or deswell in response to one or more slight changes in the environment and are therefore called 'smart' materials. It is also called stimuli responsive gel because they show sudden change in their physical structure on applying external stimulus. The external stimulus may be

(a) pH
(b) Temperature
(c) Ionic strength
(d) Electric field
(e) Intensity of light

Fig. 11.41 illustrates that at low temperature gel is in swollen form but with the increase in temperature gel shrinks due to the expulsion of water from the gel network.

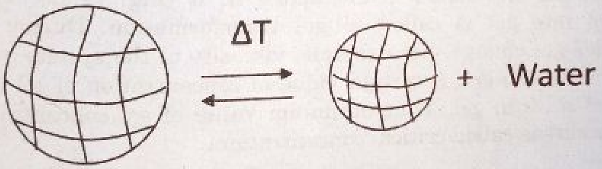


Fig. 11.41 Stimuli responsive gel

(b) Non-Responsive Gels

Non-responsive gels simply swell upon absorption of water. These gels do not show any variation in size with change in environmental stimuli.

(8) On the Basis of Stimuli

On the basis of stimuli, responsive gels can be classified as

(a) Temperature sensitive gels
(b) Electric field sensitive gels
(c) Glucose sensitive gels
(d) Ionic strength sensitive gels etc.

(9) On the Basis of Morphology

On the basis of morphology, gels can be classified as

(a) Homogenous gels

(b) Non-homogenous gels

(10) On the Basis of Additional Material

Mostly microgels contain some additional material like nanoparticles. Such microgels which possess nanoparticles are called hybrid microgels. Hybrid microgels can be classified as

(a) Microgels covered with nanoparticles

(b) Microgels filled with nanoparticles

(c) Core-shell hybrid microgels

11.23 METHODS FOR THE PREPARATION OF GELS

"The process of formation of gel by cross-linkage is called gelation". Some methods which are used for the preparation of gels are discussed below.

(1) By Coagulation Method

When solid particles are dispersed in liquid a sol system is formed. When coagulating agent (like electrolyte) is added in this sol, particles will coagulate to form a solid network and liquid is entrapped in it (Fig. 11.42). The process of conversion of sol into gel is called sol-gel transformation. During this process, physical properties get change. For example, viscosity of the system increases when system moves from sol to gel. A certain value of concentration of sol is required for transformation of sol into gel. That minimum value of sol concentration at which transformation occurs is called critical concentration.

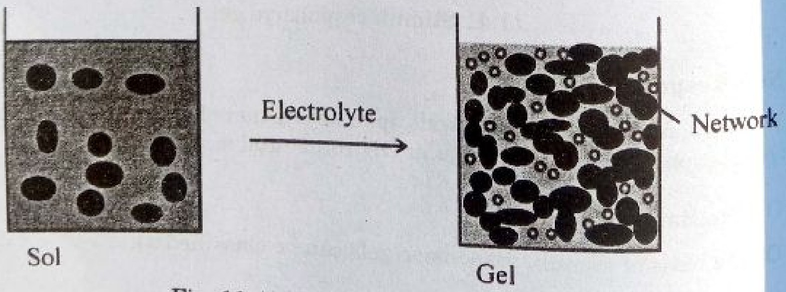


Fig. 11.42 Transformation of sol into gel

(2) By Chemical Reaction

Gel can be made by chemical reaction e.g. if two reactants A and B react with each other and two products formed are one is soluble and other is insoluble.

$$A + B \rightarrow C + D$$

Here C is insoluble product. Insoluble particle or product form sol and then, aggregate to form gel at certain concentration of sol. For example

$$BaSCN + MnSO_4 \rightarrow BaSO_4 + MnSCN$$

Barium thiocyanate	Mangnese sulfate	Barium sulfate	Mangnese thiocyanate

Here barium sulfate is water insoluble.

(3) Cooling of the Colloidal System

When colloidal system is cooled then it becomes inter-linked or cross-linked and gel is formed.

(4) Solvent Exchange

In this method one liquid in a sol is replaced with another one. If the stability of sol particles in liquid B is lower than the stability of sol in liquid A, then sol particles combine to form a crosslinked network in liquid B and gel is formed.

(5) Gelation Caused by Combination of Oppositely Charged Polyelectrolyte

Polyelectrolyte molecule may contain many ionizable pendant groups like carboxylic group (–COOH) on one chain. When -COOH ionizes, negative charge is produced on the chain. If another chain contains such group e.g. amino group that produces positive charge on the chain on protonation (Fig. 11.43). Then negative and positive charges attract each other by electrostatic force of attraction and gets aggregate to form gel.

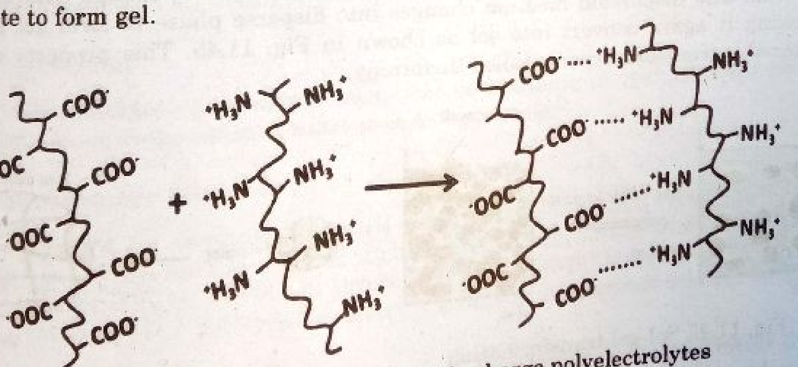


Fig. 11.43 Gel formation by oppositely charge polyelectrolytes

(6) Intra-molecular Hydrogen Bonding

Gel is also formed by intra-molecular hydrogen bonding in a molecule. In this way a large molecule is converted into cross-linked network by self bonding as shown in Fig. 11.44.

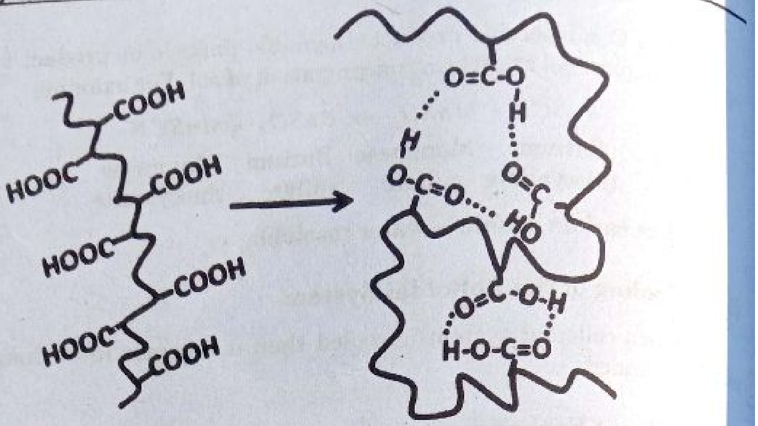


Fig. 11.44 Gel formed through intra-molecular hydrogen bonding

(7) Heating

When miceller solution is heated, micelles interlink with each other to form physical gel. The gelation in miceller solution of block copolymers of oxyethylene and oxybutylene at high temperature is an example of gel formation on heating.

11.24 PROPERTIES OF GELS

(1) Thixotropy

After a long standing time, dispersed phase of sol change into dispersion medium and dispersion medium changes into disperse phase to form gel and after shaking it again convert into sol as shown in Fig. 11.45. This property of sol-gel reversible transformation is called thixotropy.

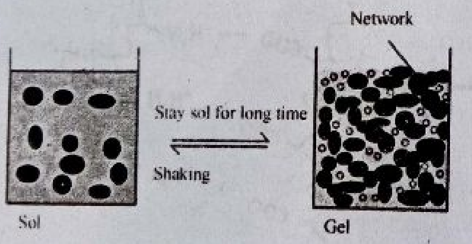


Fig. 11.45 Sol-gel transformation

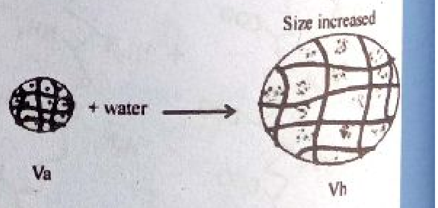


Fig. 11.46 Swelling of gel

(2) Swelling

When gel is soaked in water, then size of gel particles increases and swelling occurs as shown in Fig. 11.46.

But different forces act on it such as

(a) Osmotic pressure

(b) Cross-linking force resisting the swelling

At the stage of equilibrium

Cross-linking force = Osmotic pressure

The extent of swelling is measured in terms of swelling ratio which can be written as

$$\alpha = \frac{V_h}{V_a}$$

Where, V_h is the volume of hydrated particle in swollen state and V_a is the volume of gel particle in shrunken state.

If particle is spherical then $V_h = \frac{4}{3}\pi R_h^3$

And $V_a = \frac{4}{3}\pi R_a^3$

So, we get $\alpha = \left(\frac{R_h}{R_a}\right)^3$

If the value of α is high then the swelling ability will be higher. Rate of swelling depends upon the gel particle size if size is small then rate of swelling is high and vice-versa.

(3) De-swelling

(a) Shrinking

When water is removed from gel through some external force then size of the gel will reduce called shrinking of the gel.

(b) Syneresis

Gel undergoes a shrinkage in volume on standing in open atmosphere with the spontaneous evaporation of water is called syneresis.

(4) Responsive Behavior

Consider an example of poly(N-isopropylacrylamide) [p(N'PAM)] having coil conformation. When heat is supplied it changes its conformation from coil to globule form. The temperature-induced coil to globule transition of p(NIPAM) is shown in Fig. 11.47. The temperature at which this transition occurs is called the lower critical solution temperature (LCST).

This effect can be explained on the basis of structure of p(NIPAM) that is shown in Fig. 11.48. At low temperatures, p(NIPAM) is highly solvated due to hydrogen bonding between the amide groups on the polymer chain and the water molecules. At elevated temperatures, the hydrogen bonds between the polymer and the water molecules are broken, and intra-molecular hydrogen bonds between the C=O and N–H groups are generated leading to removal of water from the interior of polymer network. Consequently the polymer-polymer interactions become stronger than the polymer-solvent interactions at higher temperature, so polymer attains conformation of a globule.

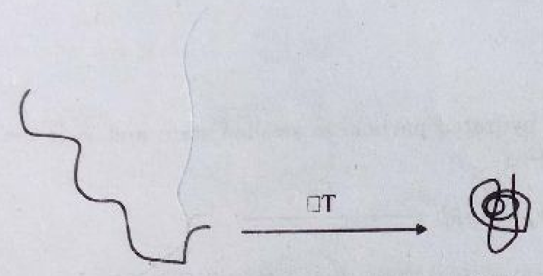


Fig. 11.47 Coil to globule transformation in p(NIPAM)

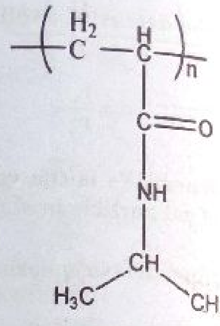


Fig. 11.48 Structure of p(NIPAM) chain

(a) Temperature Sensitivity

Such gels which show swelling or de-swelling in response to change in temperature are called thermo sensitive gels as shown in Fig. 11.50.

Thermo responsive behavior of microgels can be explained on the basis of change in hydrodynamic radius of gel particle with change in temperature. The value of hydrodynamic radius as a function of temperature for p(NIPAM) microgels as shown in Fig. 11.50. The hydrodynamic radius decreases with increase of temperature. The value of temperature at which rate of change of hydrodynamic radius with respect to temperature is maximum is called volume phase transition (VPTT). VPTT of a microgel is a function of cross-linking density and hydrophilic and hydrophobic groups present in gel network. The value of VPTT can be measured from plot of hydrodynamic radius versus temperature as shown in Fig. 11.51.

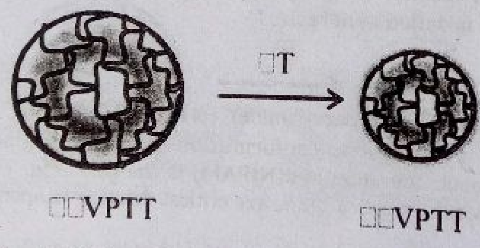


Fig. 11.50 Pictorial diagram showing temperature sensitivity of gels

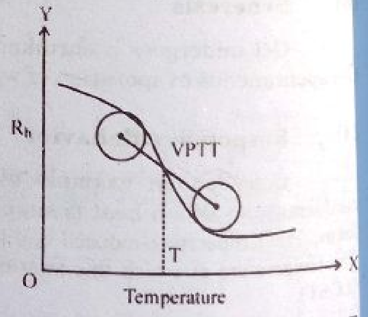


Fig. 11.51 Determination of VPTT

(b) pH Sensitivity

The cross-linked polymer microgel particles which swell or deswell when the pH approaches the pK_a/pK_b of the functional monomer incorporated inside the particles are called pH sensitive gel. The carboxylic groups become ionized with the increase in pH by adding base as shown in Fig. 11.52. As a result gel size increases due to electrostatic repulsion between similarly charged groups present in network Increase in size decreases water potential in gel. So water molecules move from medium into gel, resultantly particle size increases. Thus electrostatic repulsion and water content, both play role in increasing size of gel.

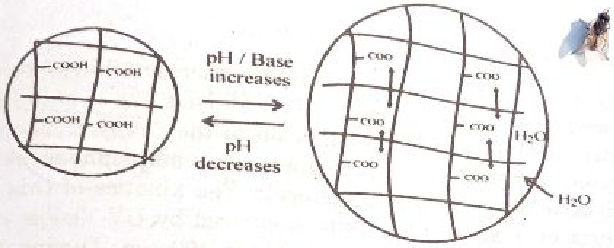


Fig. 11.52 Swelling–deswelling in pH responsive microgels

(c) Glucose Sensitivity

The microgels which respond to the variations in glucose concentration by swelling or shrinking are called glucose-responsive microgels. Such smart microgels are used for quantitative analysis of glucose in complex physiological mixtures as well as for drug delivery, especially delivery of insulin for diabetic patients.

11.25 APPLICATIONS OF GELS

(1) Drug Delivery

One of the application of gels is controlled drug delivery. The open network structure of microgels can be used to incorporate small molecules such as drugs in their interiors while their large sensitive swelling-deswelling transitions may be employed as physical and chemical triggers to direct the release of the drugs as shown in Fig. 11.53. Drug delivery depends upon the responsive behavior of gel.

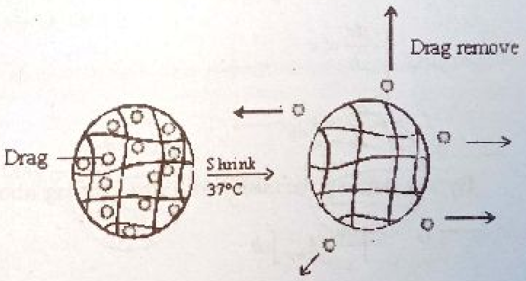


Fig. 11.53 Drug delivery

(2) Hybrid Microgels in Nanotechnology

Microgels find extensive applications in the field of nanotechnology. Microgels are used as microreactors for synthesis of different types of inorganic nanoparticles of fascinating properties and applications. Hybrid microgels are well known for their catalytic applications.

(3) Microgels in Coating Industry

Microgels play important role in improving rheological properties of paint and performance of films. That is why they are extensively used in coating industry

They impart shock resistance to the films owing to their flexible sponge-like structures.

(4) Microgels in Heterogeneous Catalysis

Recently, metal nanoparticles containing microgels have been attained a lot of attention to scientists working in the field of catalysis due to stability, durability of catalyst and open circuit for reactant diffusion to the catalyst. The catalyst can be recovered for re-use. Reduction of p-nitrophenol to p-aminophenol is widely used to study the catalytic activity of hybrid microgels. The kinetics of this reaction in the presence of hybrid microgel can be easily monitored by UV-Visible spectroscopy. p-nitrophenol in slightly basic medium absorbs at 400 nm. During the progress of reaction absorbance decreases at 400 nm due to consumption of p-nitrophenol and absorbance at 300 nm concomitantly increases with the passage of time due to increase of concentration of p-aminophenol (Fig. 11.54). Mathematical treatment of the kinetics of catalysis is given below

Let, p-nitrophenol = A, sodium borohydride = B and p-aminophenol = P

	A	+	B	$\longrightarrow$	P
$t = 0$	c_o		b_o		0
$t = t$	c		$b_o - x \approx b_o$		x

The concentration of B is taken in excess therefore, $b_0 - x \approx 0$ so,

$$-\frac{dc}{dt} \propto c$$

$$-\frac{dc}{dt} = k_{app} c$$

By separating variables and integrating above equation will be

$$-\int \frac{dc}{c} = k_{app} \int dt$$

$$-\ln c = k_{app} t + \text{constant} \qquad (11.52)$$

When $t = 0$, then $c = c_o$, by putting this approximation on above equation, we get

$$-\ln c_o = \text{constant}$$

By putting value of constant in equation (11.52), we get

$$-\ln c = k_{app} t - \ln c_o$$

$$\ln c_o - \ln c = k_{app} t$$

$$\ln\left(\frac{c_o}{c}\right) = k_{app} t \qquad (11.53)$$

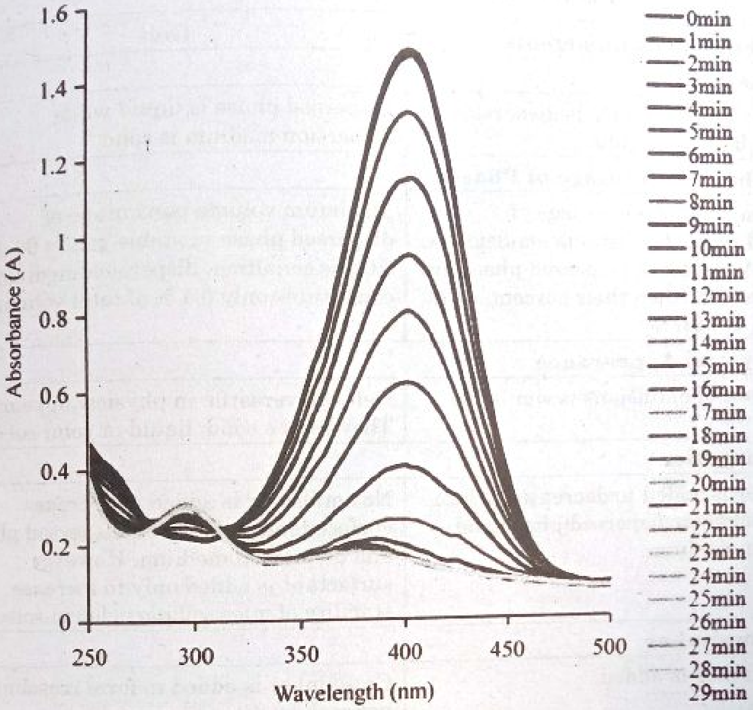


Fig. 11.54 UV-Visible spectrum of catalytic reduction of p-nitrophenol

Since,

$$A_o = \varepsilon c_o l \qquad (11.54)$$

$$A_t = \varepsilon c_t l \qquad (11.55)$$

By dividing equation (11.54) by equation (11.55), we get

$$\frac{c_o}{c_t} = \frac{A_o}{A_t}$$

By replacing the c_o/c in equation (11.53) by A_o/A_t, we get

$$\ln\left(\frac{A_o}{A_t}\right) = k_{app} t$$

$$\ln\left(\frac{A_t}{A_o}\right) = -k_{app} t \qquad (11.56)$$

This is an equation of straight line with slope $-k_{app}$. So, by plotting a graph of $\ln(A_t/A_o)$ versus t we can determine the apparent rate constant (k_{app}) from the slope.