

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 Temkin 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 physisorption.	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

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

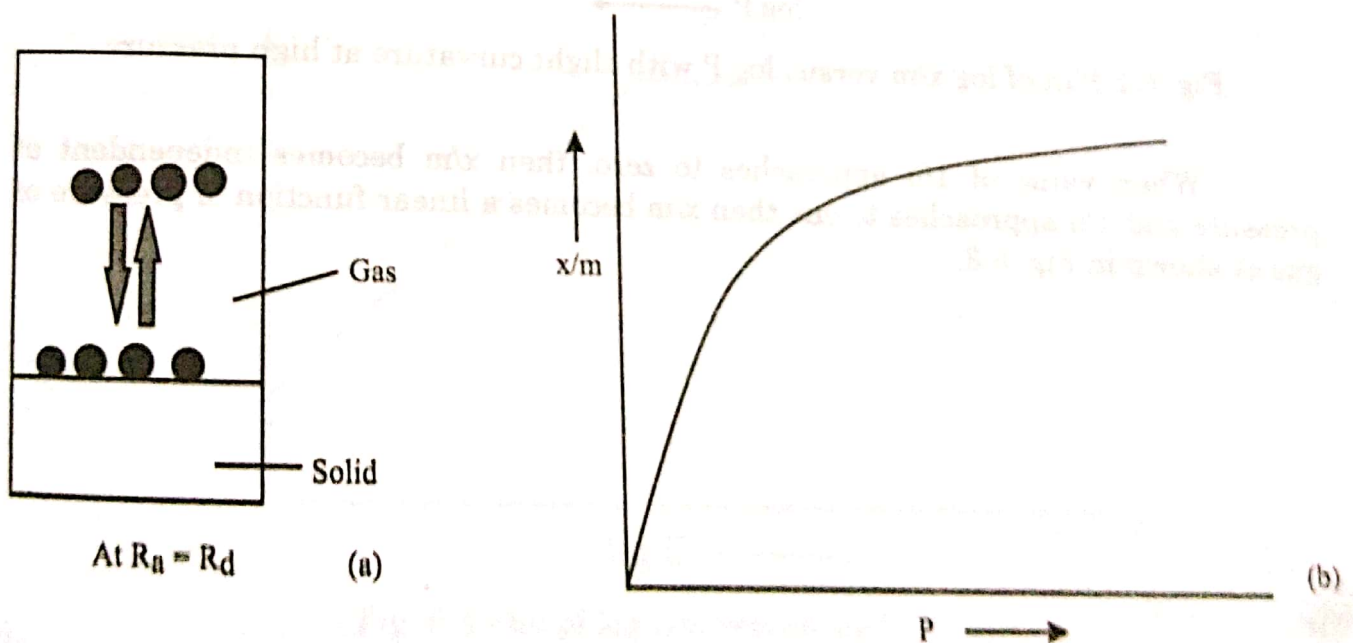


Fig. 6.1 (a) Adsorption desorption equilibrium
(b) x/m as a function of pressure of a gas at constant temperature

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

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

According to equation (6.2) $\log (x/m)$ is a linear function of $\log P$ 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 .

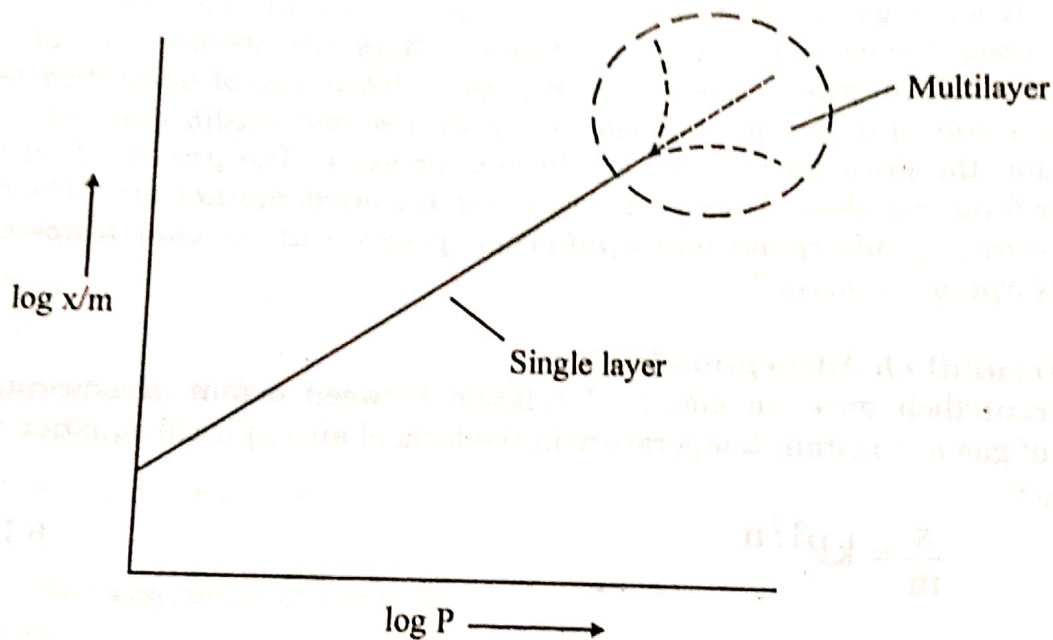


Fig. 6.2 Plot of $\log x/m$ versus $\log P$ with slight curvature at high pressure

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.

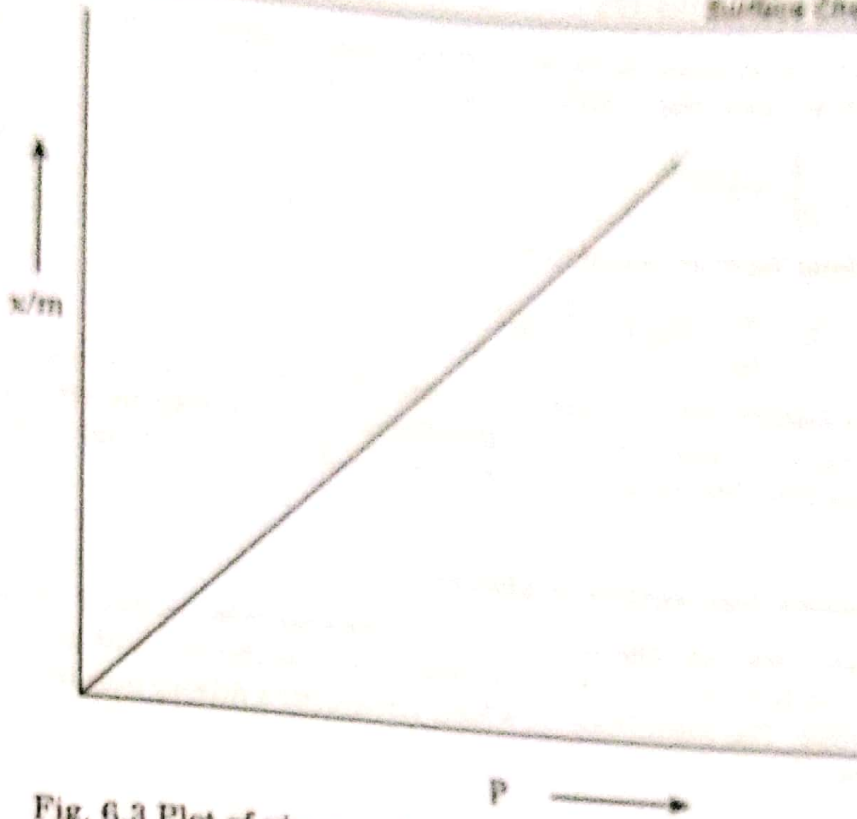


Fig. 6.3 Plot of x/m as a function of pressure when $n = 1$

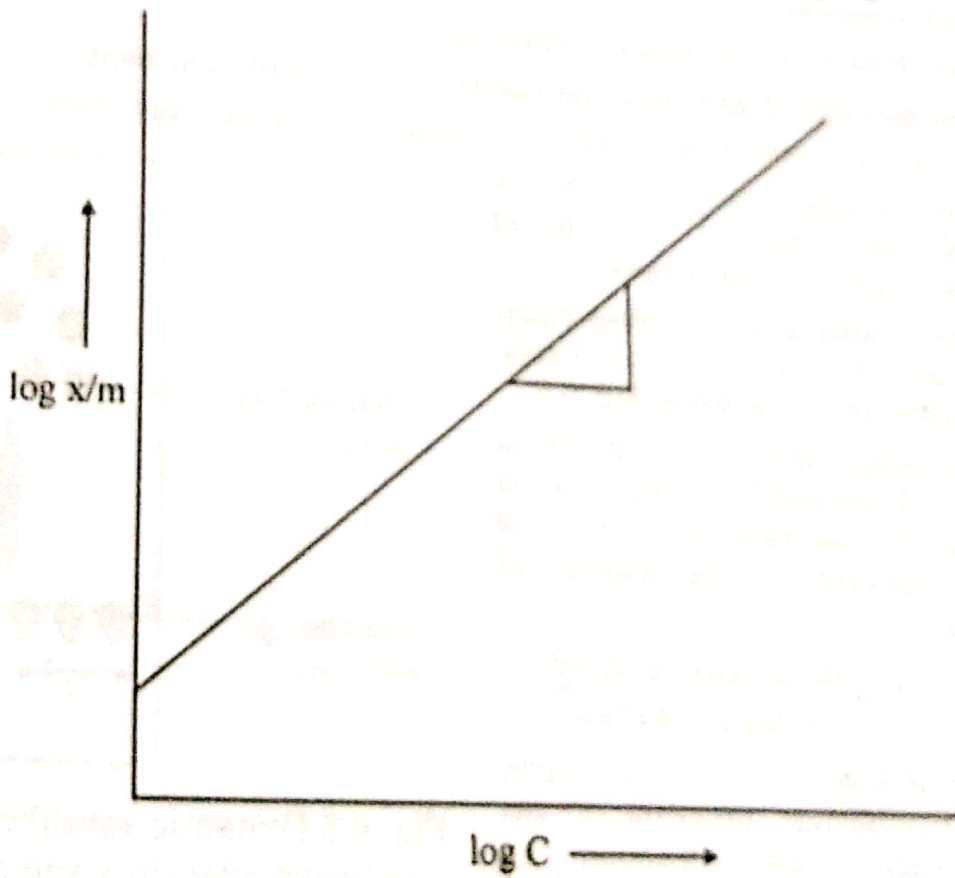


Fig. 6.4 Plot of $\log x/m$ versus $\log C$

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

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

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.

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.

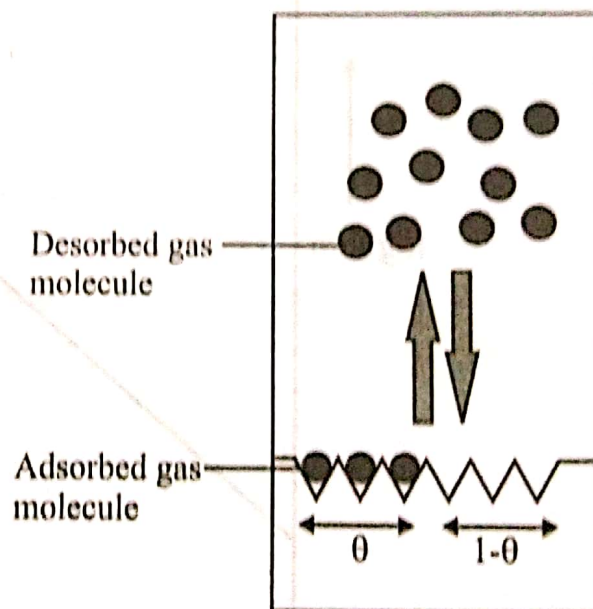


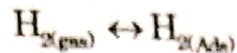
Fig. 6.5 Dynamic equilibrium exists between adsorbed and desorbed molecules

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



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

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

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

On combining equation (6.4) and (6.5)

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

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

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

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

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

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

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

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,

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

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

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

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

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

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

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

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

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

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

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

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

Putting value of $(E_{\text{Ads}} - E_{\text{Des}})$ from equation (6.10) into equation (6.9), we get

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

$$\left(\frac{b_1}{b_0}\right) e^{-\frac{\Delta H_{\text{ads}}}{RT}} = b$$

So, above equation becomes

$$\theta = \frac{bP_A}{1 + bP_A} \quad (6.11)$$

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

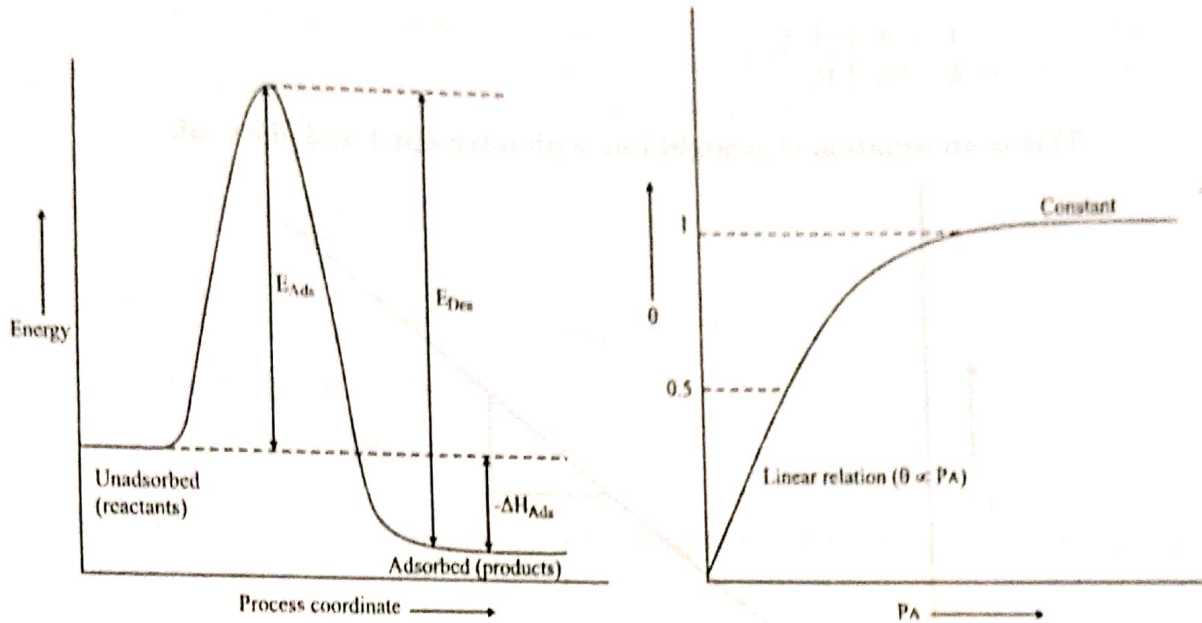


Fig. 6.6 Energy profile of adsorption and Fig. 6.7 θ as a function of pressure of gas A desorption processes

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.

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 $1/b$.

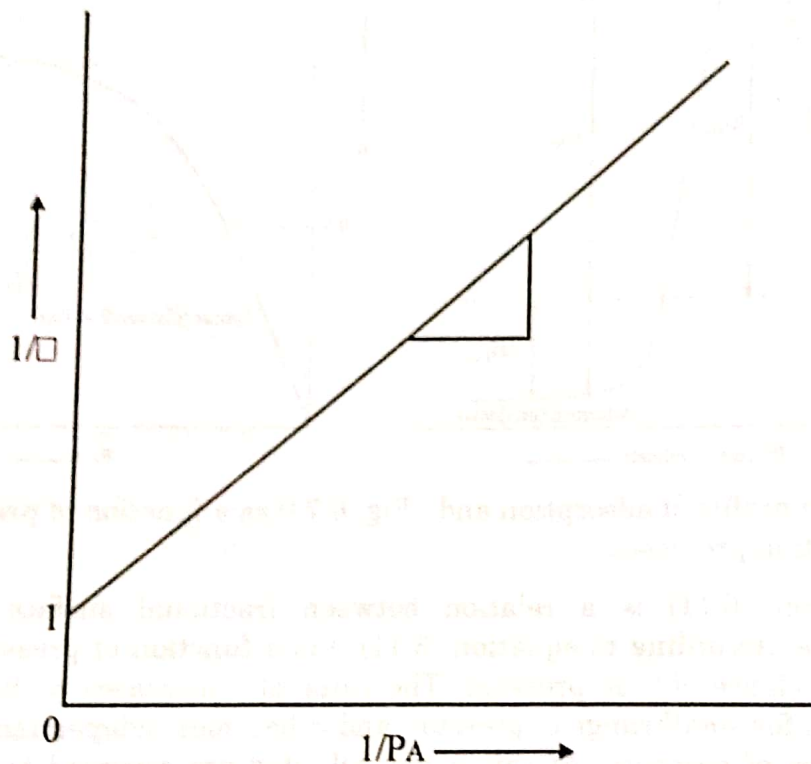


Fig. 6.8 Plot of $1/\theta$ versus $1/P_A$

Fig. 6.8 shows that $1/\theta$ 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,

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

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

So, equation (6.12) becomes

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

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

$$\begin{aligned} R_{Des} &\propto \theta^2 \\ R_{Des} &= k_{Des} \theta^2 \end{aligned} \quad (6.14)$$

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

So, equation (6.14) will become

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

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

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

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

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

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

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

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

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

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

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

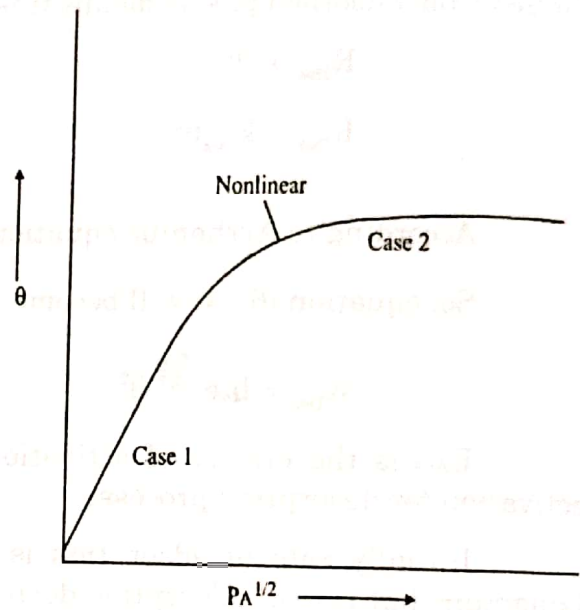
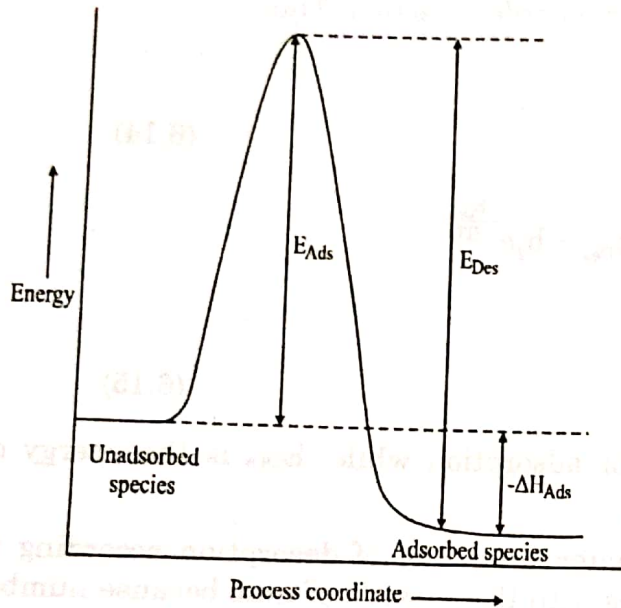


Fig. 6.9 Energy profile of adsorption of a gas Fig. 6.10 Plot of θ as a function of $P_A^{1/2}$

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

$$\Delta H_{Ads} = E_{Ads} - E_{Des} \quad (6.18)$$

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

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

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

Then equation (6.19) will become

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

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 $1 + b'P_A^{1/2} \approx b'P_A^{1/2}$. 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 $1/\theta$ 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.

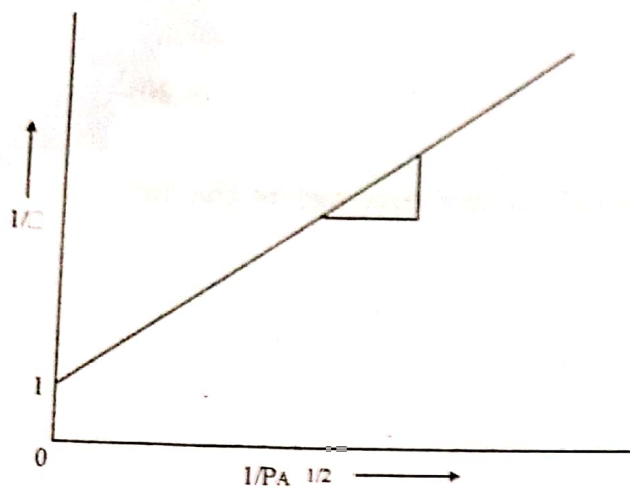


Fig. 6.11 Plot of $1/\theta$ versus $1/P_A^{1/2}$ with intercept 1

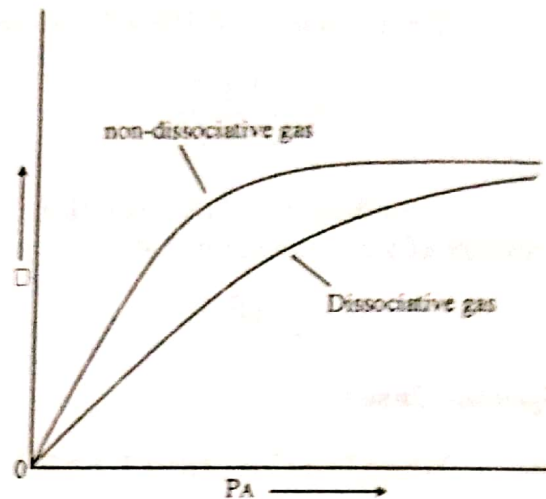


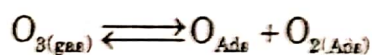
Fig. 6.12 Plot showing dependence of θ on P_A for dissociative and non-dissociative adsorption

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



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



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

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

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_s) and for the study of catalytic reaction of gas on solid surface.

6.6.1 Determination of Isosteric Enthalpy of Adsorption (ΔH_s)

The variation of pressure of a gas with temperature for a particular fractional surface coverage can be used to determine the enthalpy of adsorption called isosteric enthalpy of adsorption which is represented by ΔH_s .

We know that,

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

$$\theta(1 + bP_A) = bP_A$$

$$\theta + (bP_A)\theta = bP_A$$

$$\theta = bP_A(1 - \theta)$$

$$bP_A = \frac{\theta}{(1 - \theta)}$$

$$\theta(1 + bP_A) = bP_A$$

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

$$\theta = bP_A - (bP_A)\theta$$

$$= bP_A(1 - \theta)$$

$$\ln \theta = \ln \left(\frac{bP_A}{1 + bP_A} \right)$$

By taking natural logarithm on both sides of above equation

$$\ln(bP_A) = \ln \left(\frac{\theta}{1 - \theta} \right) \quad (6.21)$$

As $b = k_{Ads}/k_{Des}$, so b depends upon temperature because k_{Ads} and k_{Des} are dependent on temperature. Then, relation (6.21) will be

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

By differentiating above equation with respect to T at constant θ , we get

$$\left(\frac{\partial \ln P_A}{\partial T} \right)_\theta + \left(\frac{\partial \ln b}{\partial T} \right)_\theta = \frac{\partial}{\partial T} \left(\ln \frac{\theta}{1-\theta} \right)_\theta \quad (6.22)$$

As θ is constant so, $\frac{\partial}{\partial T} \left(\ln \frac{\theta}{1-\theta} \right)_\theta = 0$. Then equation (6.22) will be,

$$\begin{aligned} \left(\frac{\partial \ln P_A}{\partial T} \right)_\theta + \left(\frac{\partial \ln b}{\partial T} \right)_\theta &= 0 \\ \left(\frac{\partial \ln P_A}{\partial T} \right)_\theta &= - \left(\frac{\partial \ln b}{\partial T} \right)_\theta \end{aligned} \quad (6.23)$$

As we know that,

$$\Delta F = -RT \ln K \quad (6.24)$$

According to thermodynamics; $\Delta F = \Delta H_\theta - T\Delta S$. So, equation (6.24) will be

$$\Delta H_\theta - T\Delta S = -RT \ln b$$

$$\ln b = -\frac{\Delta H_\theta}{RT} + \frac{T\Delta S}{RT}$$

$$\ln b = -\frac{\Delta H_\theta}{RT} + \frac{\Delta S}{R}$$

Differentiating the above equation with respect to T , we get

$$\left(\frac{\partial \ln b}{\partial T} \right) = -\frac{\Delta H_\theta}{R} \frac{\partial}{\partial T} (T^{-1}) + 0$$

$$\left(\frac{\partial \ln b}{\partial T} \right) = +\frac{\Delta H_\theta}{RT^2} \quad (6.25)$$

Relation (6.25) is called Vant's Hoff equation. By putting the value of $\left(\frac{\partial \ln b}{\partial T} \right)$ from equation (6.25) in equation (6.23), we get

$$\left(\frac{\partial \ln P_A}{\partial T} \right)_\theta = -\frac{\Delta H_\theta}{RT^2}$$

$$\partial \ln P_A = -\frac{\Delta H_\theta}{R} \frac{\partial T}{T^2} \quad (6.26)$$

$$6\pi\eta r v_1 = (\rho - \rho_m) \omega^2 r^2 \left(\frac{4}{3} \pi r^3 \right)$$

$$v_1 = \frac{2(\rho - \rho_m) \omega^2 r^3}{9\eta}$$

As v_1 is the rate of change of distance with respect to time, the above equation can also be written as

$$\frac{dx}{dt} = \frac{2(\rho - \rho_m) \omega^2 r^3}{9\eta}$$

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

$$\int_{x_1}^{x_2} \frac{dx}{x} = \frac{2(\rho - \rho_m) \omega^2 r^3}{9\eta} \int_{t_1}^{t_2} dt$$

$$\ln \frac{x_2}{x_1} = \frac{2(\rho - \rho_m) \omega^2 r^3}{9\eta} (t_2 - t_1) \quad (11.5)$$

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 (11.5) 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.

11.5 SURFACTANT

"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, lyophilic colloid, finely divided solid particles and polymeric materials. Surfactants are surface active substance 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 surfactant
- (2) Non-ionic surfactant

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

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

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

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

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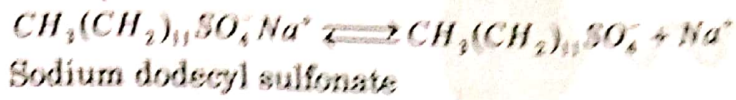
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(1) Ionic Surfactant

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



Ionic surfactant is further divided into three classes.

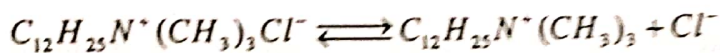
(a) Anionic Surfactants

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



(b) Cationic Surfactants

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



(c) Zwitterionic or Amphoteric Surfactant

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

(2) Non-Ionic Surfactant

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.

11.6 PROPERTIES OF SURFACTANTS

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

(1) Amphiphilic Structure

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

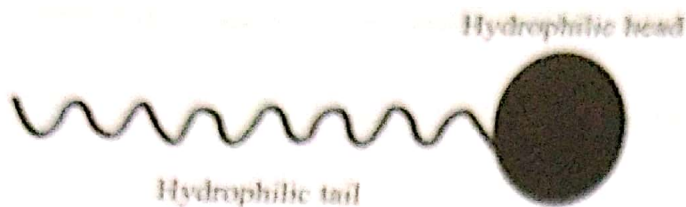


Fig. 11.11 Amphiphilic structure of surfactant.

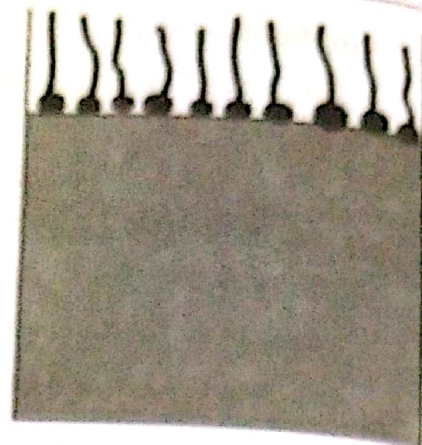


Fig. 11.12 Surfactant adsorption on air-water interfaces.

(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 hydrophilic phase and non-polar portion towards hydrophobic 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 molecule will diffuse into the bulk material and their molecules aggregate spontaneously to form a micelle as shown in Fig. 11.13.

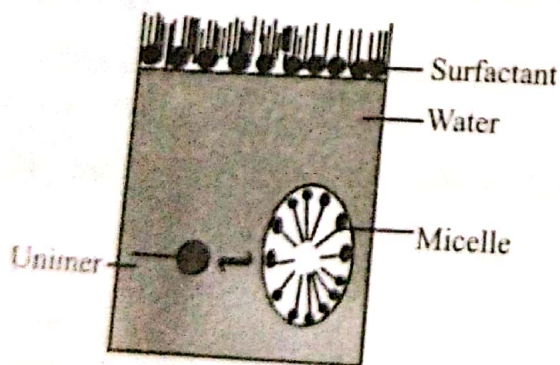


Fig. 11.13 Adsorption and micellization process

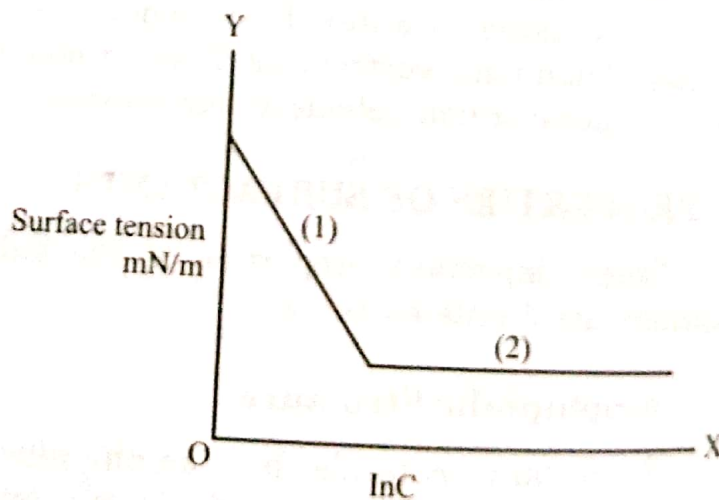


Fig. 11.14. Gibbs' adsorption isotherm

11.7 GIBBS'S ADSORPTION ISOTHERM

"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 $\ln C$ as shown in Fig. 11.14 has two regions: in region (1), surface tension decreases with the increase in value of $\ln C$. This region is called adsorption region or premicellar region and in region (2), surface tension remains constant with change of $\ln C$, this region is called micellar 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

$$\Gamma = \frac{-1}{RT} \left[\frac{d\gamma}{d \ln C} \right]_T \quad (11.6)$$

Where, Γ is surface excess concentration and its units are mole/m² 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.

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

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

By putting value of $d \ln C$ in equation (11.6), we get

$$\Gamma = \frac{-C}{RT} \left[\frac{d\gamma}{dC} \right]_T \quad (11.7)$$

$$\Gamma = \frac{-C}{2.303RT} \left[\frac{d\gamma}{d \log C} \right]_T \quad (11.8)$$

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

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 (11.6)

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

Where, $\left[\frac{d\sigma}{d \ln c} \right]$ 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

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

$$\Gamma = \frac{0.0281 \text{ Nm}^{-1}}{\text{Nmol}^{-1}} = 0.0281 \text{ mol/m}^2$$

11.8 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.

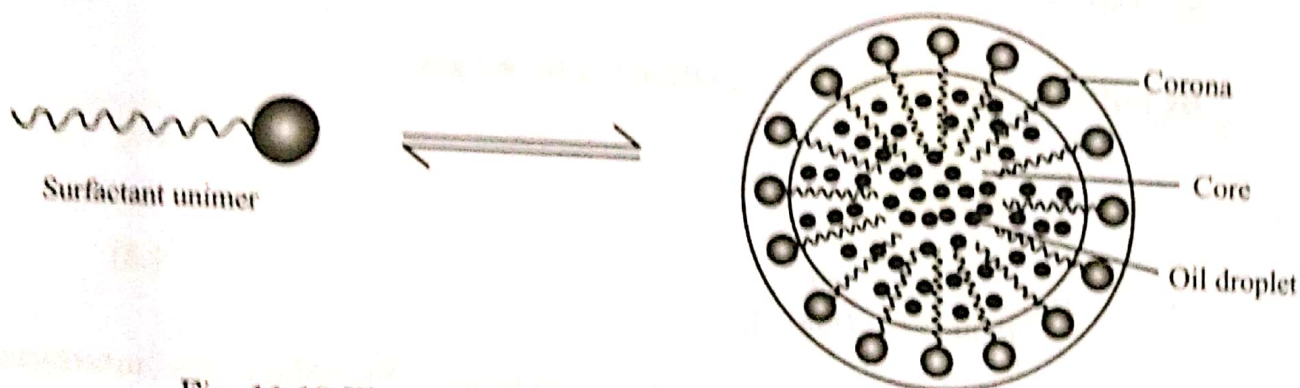


Fig. 11.15 Illustration of micellization and micelle structure

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

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 $\ln C$ 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.

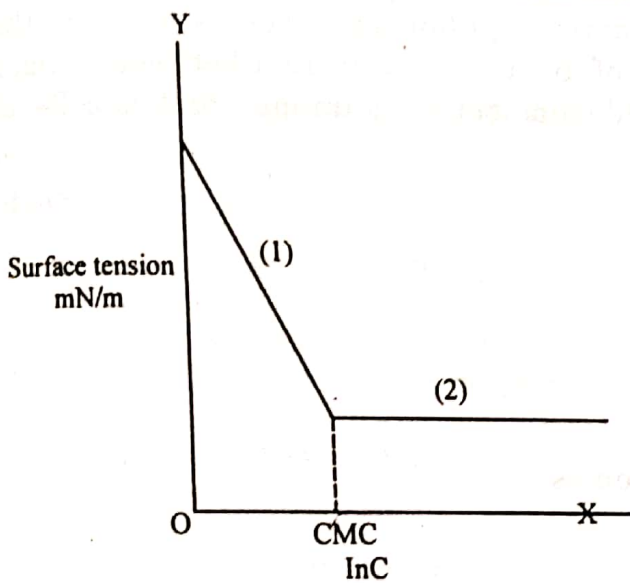


Fig. 11.16 Plot of surface tension versus $\ln C$

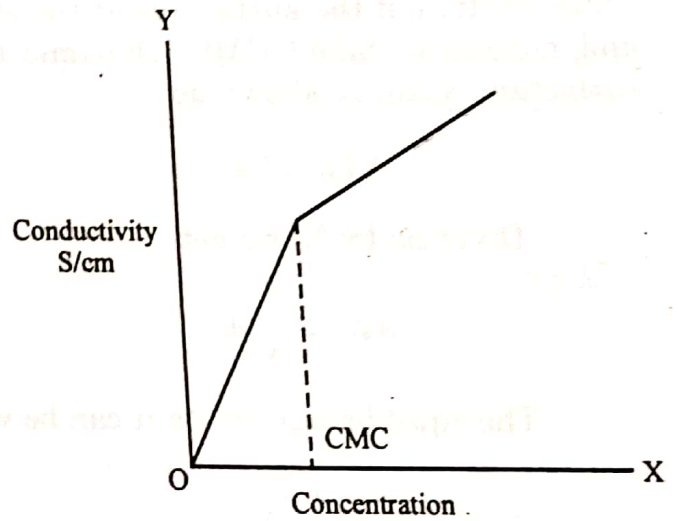
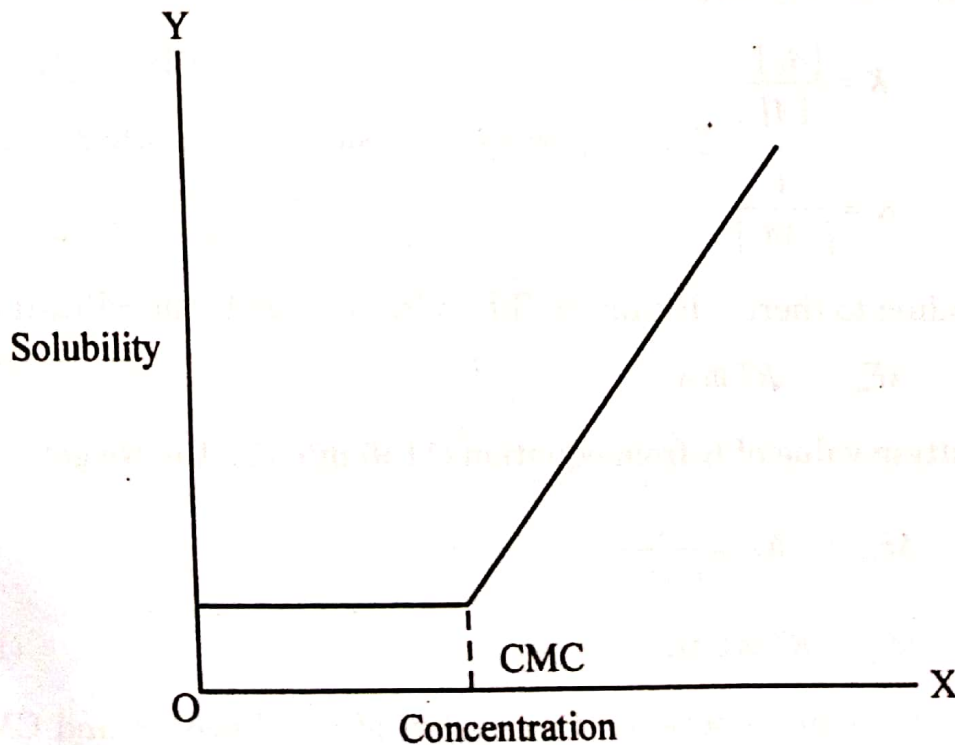


Fig. 11.17 Plot of conductivity versus concentration of surfactant



(3) Solubility

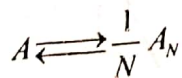
A substance is taken that is insoluble in water. Solutions of different concentrations of surfactant are prepared and the substance that is insoluble in water is added. At lower concentration of surfactant the substance is not soluble because surfactant is present at interface only. But when concentration 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.

11.9 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



Dividing by N, we get



The equilibrium constant can be written as

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

When N is very large then $1/N = 0$ and $[A] \rightarrow \text{CMC}$ then,

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

$$K = \frac{1}{[\text{CMC}]}$$

(11.9)

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

$$\Delta F_{mic} = -RT \ln K$$

(11.10)

By putting value of K from equation (11.9) into (11.10), we get

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

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

(11.11)

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 (11.10) we can find relation between $\ln CMC$ 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.

11.10 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. $\ln CMC$ is a unit less or dimensionless quantity so it is written in terms of mole fraction.

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

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 unit is KJ/mole. If ΔH_{mic} is negative then the micellization process is endothermic and if the ΔH_{mic} is positive then the process is exothermic. 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

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

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

$$\Delta F_m - T \frac{\partial \Delta F_m}{\partial T} = -RT^2 \frac{\partial \ln X_{cmc}}{\partial T} \quad (11.12)$$

According to Helmholtz equation

$$\Delta F_m - T \frac{\partial \Delta F_m}{\partial T} = \Delta H_m \quad (11.13)$$

By comparing equation (11.12) and (11.13), we get

$$\Delta H_m = -RT^2 \frac{\partial \ln X_{cmc}}{\partial T}$$

$$\frac{\Delta H_m}{RT^2} \partial T = \partial \ln X_{cmc}$$

By integrating above equation, we get

$$-\frac{\Delta H_m}{R} \int \frac{1}{T^2} \partial T = \int \partial \ln X_{cmc}$$

$$\ln X_{cmc} = \frac{\Delta H_m}{R} \left(\frac{1}{T} \right) + c \quad (11.14)$$

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

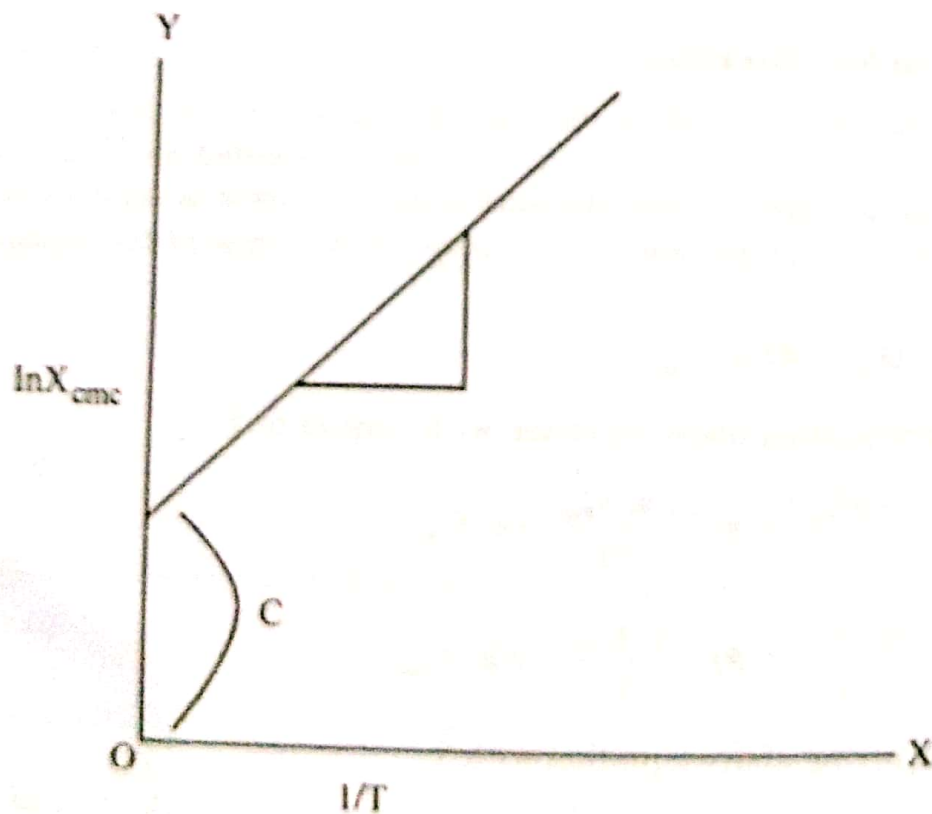


Fig. 11.19 Plot of $\ln X_{cmc}$ versus $1/T$

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 unit is $\text{JK}^{-1}\text{mole}^{-1}$. 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

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

$$\Delta S_{mic} = \frac{\Delta H_{mic} - \Delta F_{mic}}{T} \quad (11.15)$$

Example 11.2

The value of CMC of surfactant poly(oxyethylene)-poly(oxybutylene)-poly(oxyethylene) [E₂₀B₁₀E₂₀] 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

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

11.11 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 logarithm of concentration of surfactant. The value of CMC can be determined from the plot. The value of critical surface tension corresponds to CMC and 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.

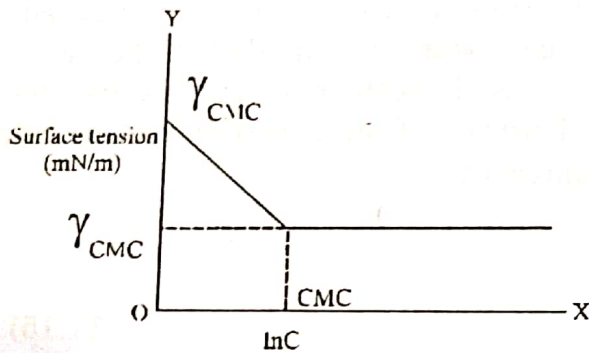
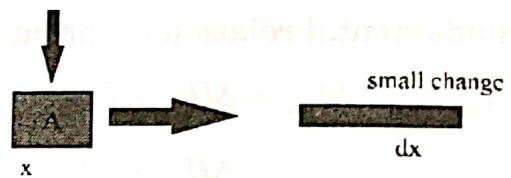
Fig. 11.20 Plot of surface tension versus $\ln C$ 

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

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

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

$$\tau \propto \gamma'$$

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

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

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 $\text{Kgm}^{-1}\text{s}^{-1}$.

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.

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

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

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_{int} can be determined and defined as "the value of reduced viscosity when concentration approaches to zero".

η_{int} 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.

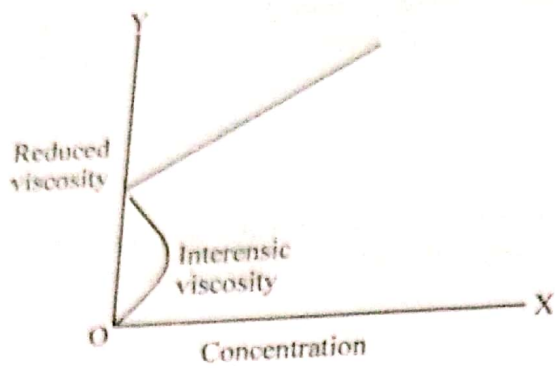


Fig. 11.22 Plot of reduced viscosity versus concentration

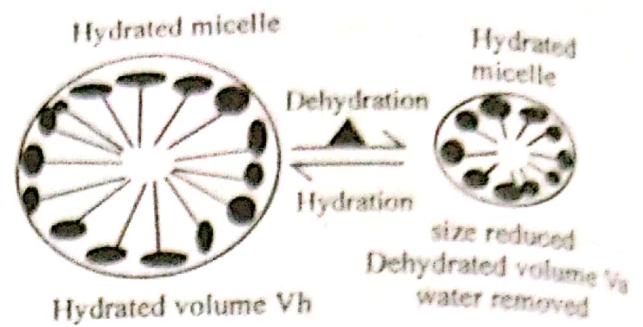


Fig. 11.23 Decrease in size of micelle due to expulsion of water

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,

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

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

$$W_h = \frac{\rho_o N_A V_a}{M_{mic}} \left(\frac{V_h}{V_a} - 1 \right) \quad (11.16)$$

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

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

By replacing $N_A V_a / M_{mic}$ with u' in equation (11.16), we get

$$W_h = u' \rho_o \left(\frac{V_h}{V_a} - 1 \right) \quad (11.17)$$

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.

$$\frac{[\eta_{mic}]}{2.5u'} = \frac{V_h}{V_a} \quad (11.18)$$

By putting value of V_h/V_a from equation (11.18) into (11.17), we get

$$W_h = v\rho_o \left(\frac{[\eta_{int}]}{2.5v'} - 1 \right)$$

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

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

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

If micelle is rigid, anhydrous and spherical then $v = \frac{[\eta_{int}]}{v'} = 2.5$

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 micellar solution.



Fig. 11.24 Scattering of light

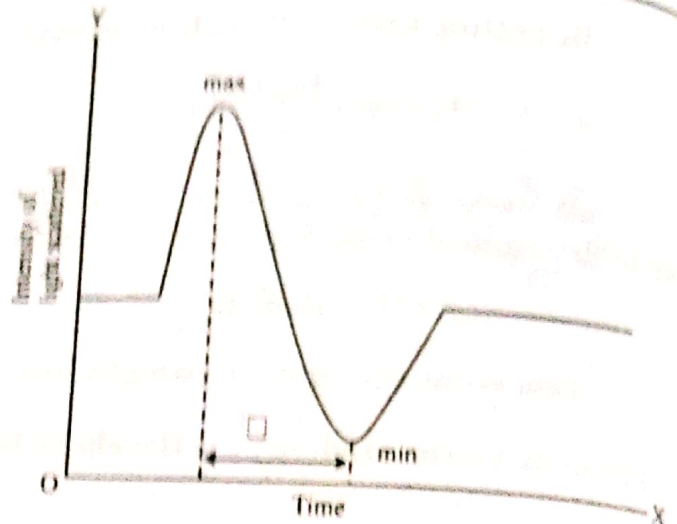


Fig. 11.25 Graph shows the variation of intensity of scattered light with change in time

Scattering vector (q) can be written as

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

Fig. 11.25 shows plot of time versus intensity of scattering light.

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

Γ is the decay rate and τ is the delayed period which is the difference between the maximum and minimum value of scattering. 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

$$D = \frac{k_B T}{6\eta\pi R_h}$$

(11.19)

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(11.19) gives the value of hydrodynamic radius.

11.12 THEORIES OF EMULSION TYPE

Theories of emulsion type fall into two categories

- (1) Qualitative Theories
- (2) Quantitative Theories