

COLLOIDS

LECTURE-6

Heterogeneous catalysis

The remainder of this chapter is devoted to developing and applying concepts of structure and reactivity in heterogeneous catalysis. For simplicity, we consider only gas/solid systems. To understand the catalytic role of a solid surface we begin by describing its unique structural features. Then, because many reactions catalysed by surfaces involve reactants and products in the gas phase, we discuss adsorption, the attachment of particles to a solid surface, and desorption, the reverse process. Finally, we consider specific mechanisms of heterogeneous catalysis.

Mechanisms of heterogeneous catalysis

Many catalysts depend on co-adsorption, the adsorption of two or more species. One consequence of the presence of a second species may be the modification of the electronic structure at the surface of a metal. For instance, partial coverage of d-metal surfaces by alkali metals has a pronounced effect on the electron distribution and reduces the work function of the metal. Such modifiers can act as promoters (to enhance the action of catalysts) or as poisons (to inhibit catalytic action).

Figure 23.29 shows the potential energy curve for a reaction influenced by the action of a heterogeneous catalyst. Differences between Fig. 23.29 and 23.1 arise from the fact that heterogeneous catalysis normally depends on at least one reactant being adsorbed (usually chemisorbed) and modified to a form in which it readily undergoes reaction, and desorption of products. Modification of the reactant often takes the form of a fragmentation of the reactant molecules. In practice, the active phase is dispersed as very small particles of linear dimension less than 2 nm on a porous oxide support. Shape-selective catalysts, such as the zeolites (*Impact 123.1*), which have a pore size that can distinguish shapes and sizes at a molecular scale, have high internal specific surface areas, in the range of 100–500 m² g⁻¹.

The decomposition of phosphine (PH₃) on tungsten is first-order at low pressures and zeroth-order at high pressures. To account for these observations, we write down a plausible rate law in terms of an adsorption isotherm and explore its form in the limits of high and low pressure. If the rate is supposed to be proportional to the surface coverage and we suppose that θ is given by the Langmuir isotherm, we would write

$$v = k_r \theta = \frac{k_r K p}{1 + K p} \quad (23.26)$$

where p is the pressure of phosphine. When the pressure is so low that $Kp \ll 1$, we can neglect Kp in the denominator and obtain

$$v = k_r K p \quad (23.27a)$$

and the decomposition is first-order. When $Kp \gg 1$, we can neglect the 1 in the denominator, whereupon the Kp terms cancel and we are left with

$$v = k_r \quad (23.27b)$$

and the decomposition is zeroth-order.

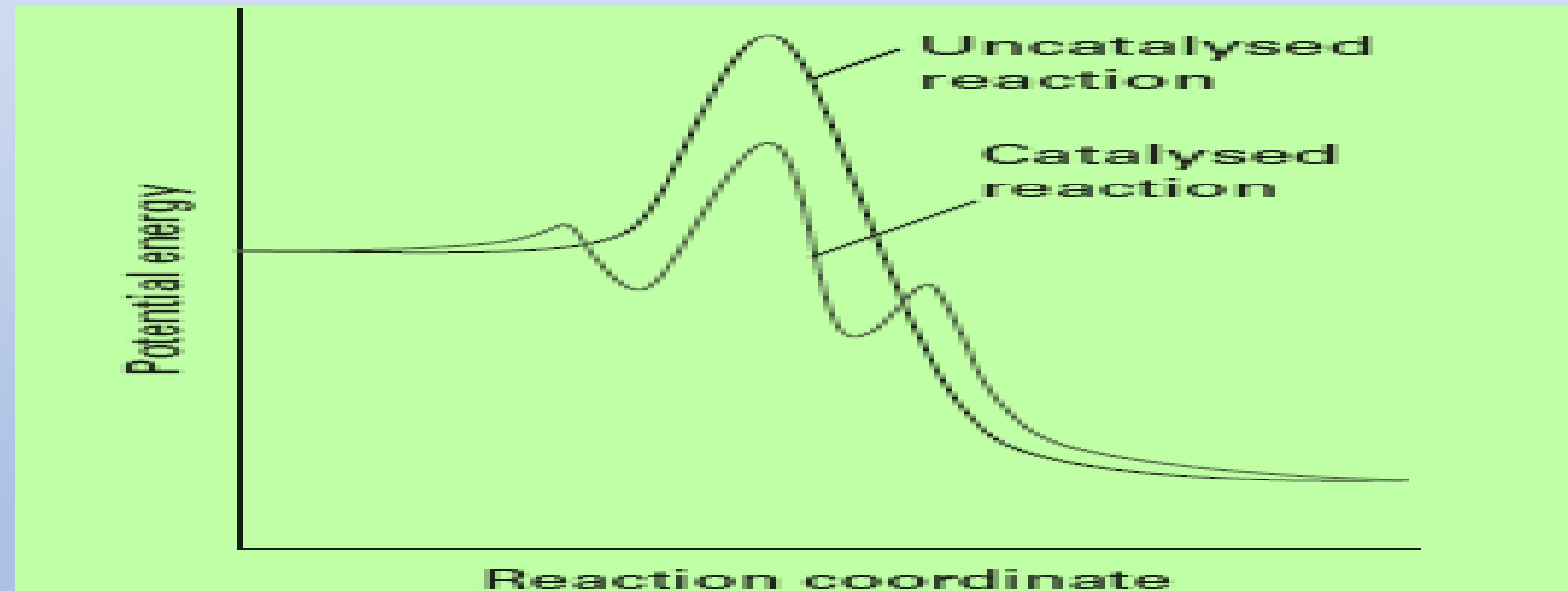


Fig. 23.29 The reaction profile for catalysed and uncatalysed reactions. The catalysed reaction path includes activation energies for adsorption and desorption as well as an overall lower activation energy for the process.

In the Langmuir–Hinshelwood mechanism (LH mechanism) of surface-catalysed reactions, the reaction takes place by encounters between molecular fragments and atoms adsorbed on the surface. We therefore expect the rate law to be second-order in the extent of surface coverage:



Insertion of the appropriate isotherms for A and B then gives the reaction rate in terms of the partial pressures of the reactants. For example, if A and B follow Langmuir isotherms, and adsorb without dissociation, so that

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B} \quad \theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B} \quad (23.29)$$

then it follows that the rate law is

$$v = \frac{k_T K_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B)^2} \quad (23.30)$$

The rate law according to the Langmuir–Hinshelwood mechanism

The parameters K in the isotherms and the rate constant k_T are all temperature-dependent, so the overall temperature dependence of the rate may be strongly non-Arrhenius (in the sense that the reaction rate is unlikely to be proportional to $e^{-E_a/RT}$). The Langmuir–Hinshelwood mechanism is dominant for the catalytic oxidation of CO to CO₂.

In the Eley–Rideal mechanism (ER mechanism) of a surface-catalysed reaction, a gas-phase molecule collides with another molecule already adsorbed on the surface. The rate of formation of product is expected to be proportional to the partial pressure, p_B , of the non-adsorbed gas B and the extent of surface coverage, θ_A , of the adsorbed gas A. It follows that the rate law should be



The rate constant, k_T , might be much larger than for the uncatalysed gas-phase reaction because the reaction on the surface has a low activation energy and the adsorption itself is often not activated.

If we know the adsorption isotherm for A, we can express the rate law in terms of its partial pressure, p_A . For example, if the adsorption of A follows a Langmuir isotherm in the pressure range of interest, then the rate law would be

$$v = \frac{k_T K p_A p_B}{1 + K p_A}$$

The rate law according to the Eley-Rideal mechanism	(23.32)
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If A were a diatomic molecule that adsorbed as atoms, we would substitute the isotherm given in eqn 23.14 instead.

According to eqn 23.32, when the partial pressure of A is high (in the sense $K p_A \gg 1$) there is almost complete surface coverage, and the rate is equal to $k_T p_B$. Now the rate-determining step is the collision of B with the adsorbed fragments. When the pressure of A is low $K p_A \ll 1$, perhaps because of its reaction, the rate is equal to $k_T K p_A p_B$; now the extent of surface coverage is important in the determination of the rate.

Almost all thermal surface-catalysed reactions are thought to take place by the LH mechanism, but a number of reactions with an ER mechanism have also been identified from molecular beam investigations. For example, the reaction between H(g) and D(ad) to form HD(g) is thought to be by an ER mechanism involving the direct collision and pick-up of the adsorbed D atom by the incident H atom. However, the two mechanisms should really be thought of as ideal limits, and all reactions lie somewhere between the two and show features of each one.

Colloids

A **colloid**, or **disperse phase**, is a dispersion of small particles of one material in another that does not settle out under gravity. In this context, 'small' means that one dimension at least is smaller than about 500 nm in diameter (about the wavelength of visible light). Many colloids are suspensions of nanoparticles (particles of diameter up to about 100 nm). In general, colloidal particles are aggregates of numerous atoms or molecules, but are commonly but not universally too small to be seen with an ordinary optical microscope. They pass through most filter papers, but can be detected by light-scattering and sedimentation.

Classification and preparation

The name given to the colloid depends on the two phases involved. A **sol** is a dispersion of a solid in a liquid (such as clusters of gold atoms in water) or of a solid in a solid (such as ruby glass, which is a gold-in-glass sol, and achieves its colour by light scattering). An **aerosol** is a dispersion of a liquid in a gas (like fog and many sprays) or a solid in a gas (such as smoke): the particles are often large enough to be seen with a microscope. An **emulsion** is a dispersion of a liquid in a liquid (such as milk). A **foam** is a dispersion of a gas in a liquid.

A further classification of colloids is as **lyophilic**, or solvent attracting, and **lyophobic**, solvent repelling. If the solvent is water, the terms **hydrophilic** and **hydrophobic**, respectively, are used instead. Lyophobic colloids include the metal sols. Lyophilic colloids generally have some chemical similarity to the solvent, such as $-OH$ groups able to form hydrogen bonds. A **gel** is a semirigid mass of a lyophilic sol.

The preparation of aerosols can be as simple as sneezing (which produces an imperfect aerosol). Laboratory and commercial methods make use of several techniques. Material (for example, quartz) may be ground in the presence of the dispersion medium. Passing a heavy electric current through a cell may lead to the sputtering (crumbling) of an electrode into colloidal particles. Arcing between electrodes immersed in the support medium also produces a colloid. Chemical precipitation sometimes results in a colloid. A precipitate (for example, silver iodide) already formed may be dispersed by the addition of a peptizing agent (for example, potassium iodide). Clays may be peptized by alkalis, the OH ion being the active agent.

Emulsions are normally prepared by shaking the two components together vigorously, although some kind of emulsifying agent usually has to be added to stabilize the product. This emulsifying agent may be a soap (the salt of a long-chain carboxylic acid) or other surfactant (surface active) species, or a lyophilic sol that forms a protective film around the dispersed phase. In milk, which is an emulsion of fats in water, the emulsifying agent is casein, a protein containing phosphate groups. It is clear from the formation of cream on the surface of milk that casein is not completely successful in stabilizing milk: the dispersed fats coalesce into oily droplets which float to the surface. This coagulation may be prevented by ensuring that the emulsion is dispersed very finely initially: intense agitation with ultrasonics brings this dispersion about, the product being 'homogenized' milk.

One way to form an aerosol is to tear apart a spray of liquid with a jet of gas. The dispersal is aided if a charge is applied to the liquid, for then electrostatic repulsions help to blast it apart into droplets. This procedure may also be used to produce emulsions, for the charged liquid phase may be directed into another liquid.

Colloids are often purified by dialysis (*Impact 15.1*). The aim is to remove much (but not all, for reasons explained later) of the ionic material that may have accompanied their formation. A membrane (for example, cellulose) is selected that is permeable to solvent and ions, but not to the colloid particles. Dialysis is very slow, and is normally accelerated by applying an electric field and making use of the charges carried by many colloidal particles; the technique is then called **electrodialysis**.

Structure and stability

Colloids are thermodynamically unstable with respect to the bulk. This instability can be expressed thermodynamically by noting that because the change in Helmholtz energy, dA , when the surface area of the sample changes by $d\sigma$ at constant temperature and pressure is $dA = \gamma d\sigma$, where γ is the interfacial surface tension (Section 17.8a), it follows that $dA < 0$ if $d\sigma < 0$. The survival of colloids must therefore be a consequence of the kinetics of collapse: colloids are thermodynamically unstable but kinetically nonlabile.

At first sight, even the kinetic argument seems to fail: colloidal particles attract each other over large distances, so there is a long-range force that tends to condense them into a single blob. The reasoning behind this remark is as follows. The energy of attraction between two individual atoms i and j separated by a distance R_{ij} , one in each colloidal particle, varies with their separation as $1/R_{ij}^6$ (Section 17.5). The sum of all these pairwise interactions, however, decreases only as approximately $1/R^2$ (the precise variation depending on the shape of the particles and their closeness), where R is the separation of the centres of the particles. The change in the power from 6 to 2 stems from the fact that at short distances only a few molecules interact but at large distances many individual molecules are at about the same distance from one another, and contribute equally to the sum (Fig. 18.21), so the total interaction does not fall off as fast as the single molecule–molecule interaction.

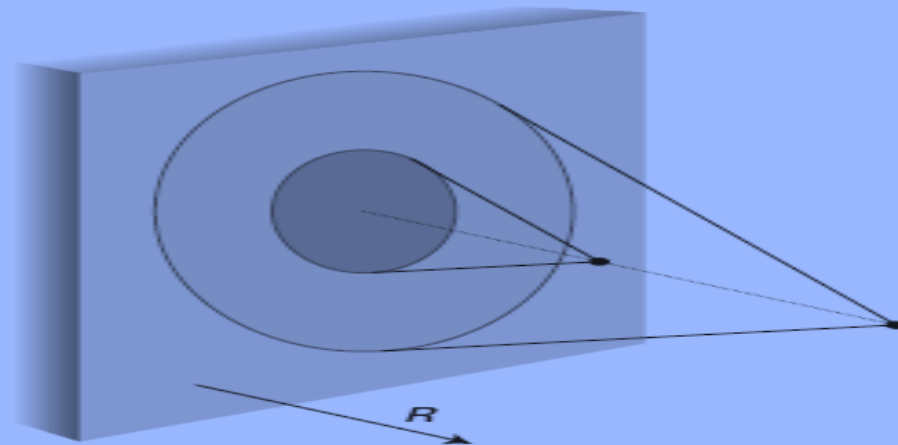


Fig. 18.21 Although the attraction between individual molecules is proportional to $1/R^6$, more molecules are within range at large separations (pale region) than at small separation (dark region), so the total interaction energy declines more slowly and is proportional to a lower power of R .

Several factors oppose the long-range dispersion attraction. For example, there may be a protective film at the surface of the colloid particles that stabilizes the interface and cannot be penetrated when two particles touch. Thus the surface atoms of a platinum sol in water react chemically and are turned into $-\text{Pt}(\text{OH})_3\text{H}_3$, and this layer encases the particle like a shell. A fat can be emulsified by a soap because the long hydrocarbon tails penetrate the oil droplet but the carboxylate head groups (or other hydrophilic groups in synthetic detergents) surround the surface, form hydrogen bonds with water, and give rise to a shell of negative charge that repels a possible approach from another similarly charged particle.

The electrical double layer

A major source of kinetic nonlability of colloids is the existence of an electric charge on the surfaces of the particles. On account of this charge, ions of opposite charge tend to cluster nearby, and an ionic atmosphere is formed, just as for ions (Section 5.13).

We need to distinguish two regions of charge. First, there is a fairly immobile layer of ions that adhere tightly to the surface of the colloidal particle, and which may include water molecules (if that is the support medium). The radius of the sphere that captures this rigid layer is called the **radius of shear** and is the major factor determining the mobility of the particles. The electric potential at the radius of shear relative to its value in the distant, bulk medium is called the **zeta potential**, ζ , or the **electrokinetic potential**. Second, the charged unit attracts an oppositely charged atmosphere of mobile ions. The inner shell of charge and the outer ionic atmosphere is called the **electrical double layer**.

The theory of the stability of lyophobic dispersions was developed by B. Derjaguin and L. Landau and independently by E. Verwey and J.T.G. Overbeek, and is known as the **DLVO theory**.¹ It assumes that there is a balance between the repulsive interaction between the charges of the electrical double layers on neighbouring particles and the attractive interactions arising from van der Waals interactions between the molecules in the particles. The potential energy arising from the repulsion of double layers on particles of radius a has the form

$$V_{\text{repulsion}} = +\frac{Aa^2\zeta^2}{R}e^{-s/r_D} \quad (18.14)$$

where A is a constant, ζ is the zeta potential, R is the separation of centres, s is the separation of the surfaces of the two particles ($s = R - 2a$ for spherical particles of radius a), and r_D is the thickness of the double layer. This expression is valid for small particles with a thick double layer ($a \ll r_D$). When the double layer is thin ($r_D \ll a$), the expression is replaced by

$$V_{\text{repulsion}} = \frac{1}{2} A a \zeta^2 \ln(1 + e^{-s/r_D}) \quad (18.15)$$

In each case, the thickness of the double layer can be estimated from an expression like that derived for the thickness of the ionic atmosphere in the Debye–Hückel theory (eqn 5.91) in which there is a competition between the assembling influences of the attraction between opposite charges and the disruptive effect of thermal motion:

$$r_D = \left(\frac{\epsilon RT}{2\rho F^2 I b^\ominus} \right)^{1/2} \quad \boxed{\text{Thickness of the electrical double layer}} \quad (18.16)$$

where I is the ionic strength of the solution, ρ its mass density, and $b^\ominus = 1 \text{ mol kg}^{-1}$ (F is Faraday's constant and ϵ is the permittivity, $\epsilon = \epsilon_r \epsilon_0$). The potential energy arising from the attractive interaction has the form

$$V_{\text{attraction}} = -\frac{B}{s} \quad (18.17)$$

where B is another constant. The variation of the total potential energy with separation is shown in Fig. 18.22.

At high ionic strengths, the ionic atmosphere is dense and the potential shows a secondary minimum at large separations. Aggregation of the particles arising from the stabilizing effect of this secondary minimum is called **flocculation**. The flocculated material can often be redispersed by agitation because the well is so shallow. **Coagulation**, the irreversible aggregation of distinct particles into large particles, occurs when the separation of the particles is so small that they enter the primary minimum of the potential energy curve and van der Waals forces are dominant.

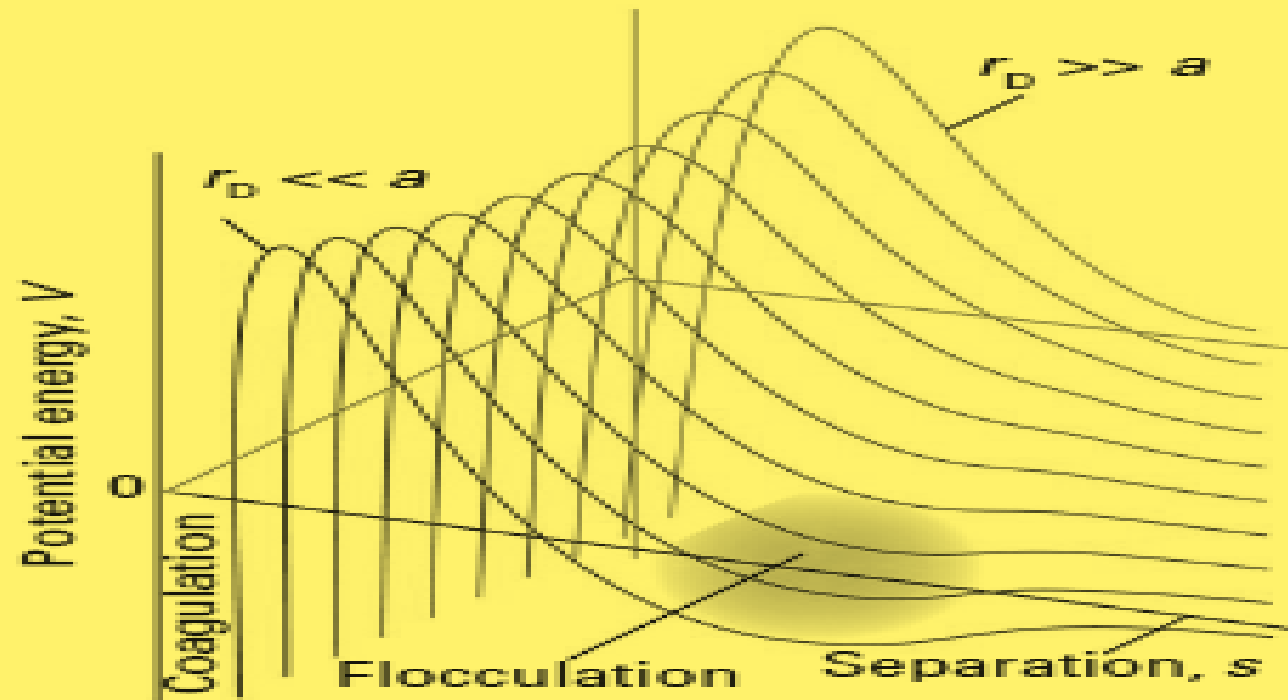
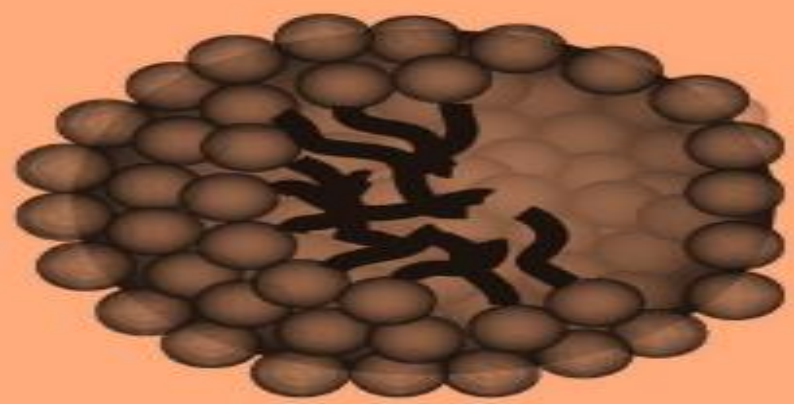


Fig. 18.22 The potential energy of interaction as a function of the separation of the centres of the two particles and its variation with the ratio of the particle size (radius a for spherical particles) to the thickness of the electrical double layer, r_D . The regions labelled coagulation and flocculation show the dips in the potential energy curves where these processes occur.

The ionic strength is increased by the addition of ions, particularly those of high charge type, so such ions act as flocculating agents. This increase is the basis of the empirical Schulze–Hardy rule, that hydrophobic colloids are flocculated most efficiently by ions of opposite charge type and high charge number. The Al^{3+} ions in alum are very effective, and are used to induce the congealing of blood. When river water containing colloidal clay flows into the sea, the salt water induces flocculation and coagulation, and is a major cause of silting in estuaries. Metal oxide sols tend to be positively charged, whereas sulfur and the noble metals tend to be negatively charged.

The primary role of the electric double layer is to confer kinetic non-lability. Colliding colloidal particles break through the double layer and coalesce only if the collision is sufficiently energetic to disrupt the layers of ions and solvating molecules, or if thermal motion has stirred away the surface accumulation of charge. This disruption may occur at high temperatures, which is one reason why sols precipitate when they are heated.

Micelles and biological membranes



In aqueous solutions surfactant molecules or ions can cluster together as micelles, which are colloid-sized clusters of molecules, for their hydrophobic tails tend to congregate (through hydrophobic interactions—see Section 17.5f), and their hydrophilic head groups provide protection (Fig. 18.23).

Fig. 18.23 A schematic version of a spherical micelle. The hydrophilic groups are represented by spheres and the hydrophobic hydrocarbon chains are represented by the stalks; these stalks are mobile.

Micelle formation

Micelles form only above the critical micelle concentration (CMC) and above the Krafft temperature. The CMC is detected by noting a pronounced change in physical properties of the solution, particularly the molar conductivity (Fig. 18.24). There is no abrupt change in properties at the CMC; rather, there is a transition region corresponding to a range of concentrations around the CMC where physical properties vary smoothly but nonlinearly with the concentration. The hydrocarbon interior of a micelle is like a droplet of oil. Nuclear magnetic resonance shows that the hydrocarbon

tails are mobile, but slightly more restricted than in the bulk. Micelles are important in industry and biology on account of their solubilizing function: matter can be transported by water after it has been dissolved in their hydrocarbon interiors. For this reason, micellar systems are used as detergents, for organic synthesis, froth flotation, and petroleum recovery.

Non-ionic surfactant molecules may cluster together in clumps of 1000 or more, but ionic species tend to be disrupted by the electrostatic repulsions between head groups and are normally limited to groups of less than about 100. However, the disruptive effect depends more on the effective size of the head group than the charge. For example, ionic surfactants such as sodium dodecyl sulfate (SDS) and cetyl trimethylammonium bromide (CTAB) form rods at moderate concentrations, whereas sugar surfactants form small, approximately spherical micelles. The micelle population is often polydisperse, and the shapes of the individual micelles vary with shape of the constituent surfactant molecules, surfactant concentration, and temperature. A useful predictor of the shape of the micelle is the surfactant parameter, N_s , defined as

$$N_s = \frac{V}{Al}$$

Definition of the surfactant parameter

[18.18]

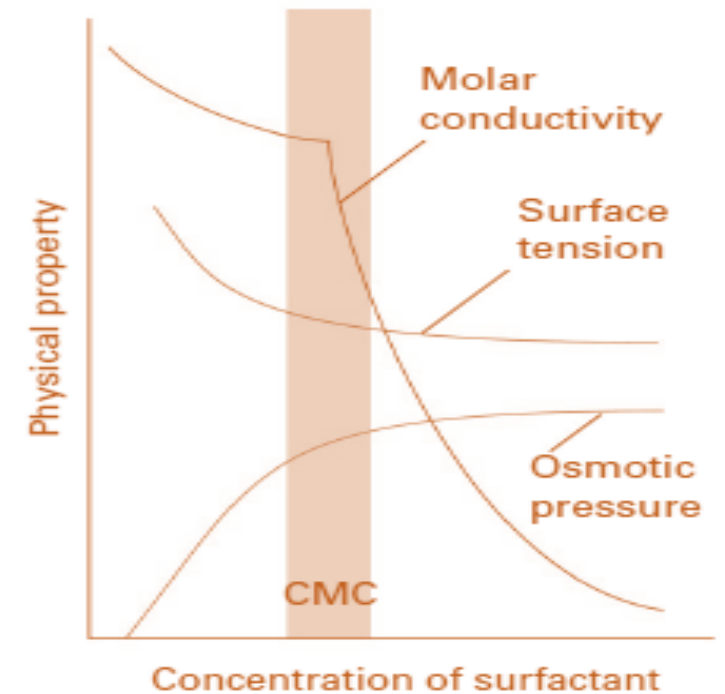


Fig. 18.24 The typical variation of some physical properties of an aqueous solution of sodium dodecylsulfate close to the critical micelle concentration (CMC).

where V is the volume of the hydrophobic surfactant tail, A is the area of the hydrophilic surfactant head group, and l is the maximum length of the surfactant tail. Table 18.1 summarizes the dependence of aggregate structure on the surfactant parameter.

In aqueous solutions spherical micelles form, as shown in Fig. 18.23, with the polar head groups of the surfactant molecules on the micellar surface and interacting favorably with solvent and ions in solution. Hydrophobic interactions stabilize the aggregation of the hydrophobic surfactant tails in the micellar core. Under certain experimental conditions, a liposome may form, with an inward pointing inner surface of molecules surrounded by an outward pointing outer layer (Fig. 18.25). Liposomes may be used to carry nonpolar drug molecules in blood.

Increasing the ionic strength of the aqueous solution reduces repulsions between surface head groups, and cylindrical micelles can form. These cylinders may stack together in reasonably close-packed (hexagonal) arrays, forming lyotropic mesomorphs and, more colloquially, ‘liquid crystalline phases’.

Reverse micelles form in nonpolar solvents, with small polar surfactant head groups in a micellar core and more voluminous hydrophobic surfactant tails extending into the organic bulk phase. These spherical aggregates can solubilize water in organic solvents by creating a pool of trapped water molecules in the micellar core. As aggregates arrange at high surfactant concentrations to yield long-range positional order, many other types of structures are possible including cubic and hexagonal shapes.

The enthalpy of micelle formation reflects the contributions of interactions between micelle chains within the micelles and between the polar head groups and the

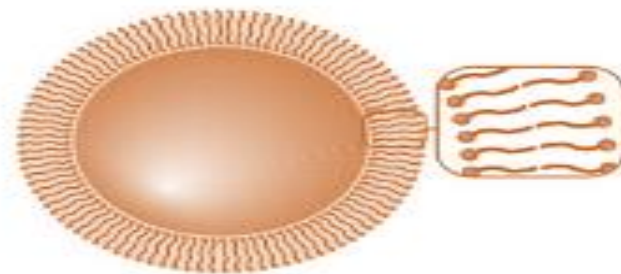


Fig. 18.25 The cross-sectional structure of a spherical liposome.

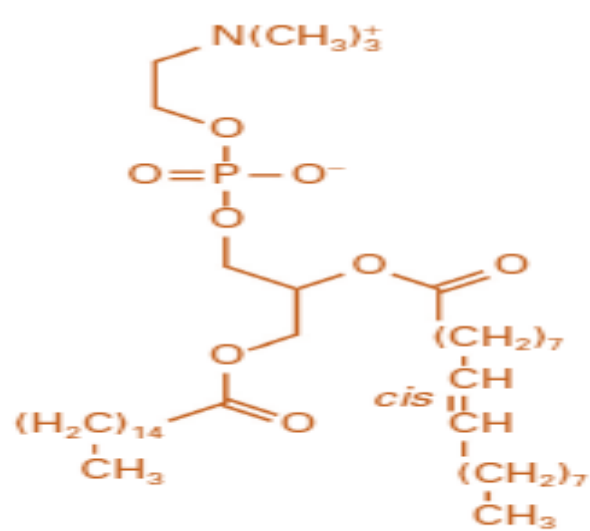
Table 18.1 Variation of micelle shape with the surfactant parameter

Value or range of the surfactant parameter, N_s	Micelle shape
< 0.33	Spherical
0.33 to 0.50	Cylindrical rods
0.50 to 1.00	Vesicles
1.00	Planar bilayers
> 1.00	Reverse micelles and other shapes

surrounding medium. Consequently, enthalpies of micelle formation display no readily discernible pattern and may be positive (endothermic) or negative (exothermic). Many non-ionic micelles form endothermically, with ΔH of the order of 10 kJ per mole of surfactant molecules. That such micelles do form above the CMC indicates that the entropy change accompanying their formation must then be positive, and measurements suggest a value of about $+140 \text{ J K}^{-1} \text{ mol}^{-1}$ at room temperature. The fact that the entropy change is positive even though the molecules are clustering together shows that hydrophobic interactions are important in the formation of micelles.

Bilayers, vesicles, and membranes

Some micelles at concentrations well above the CMC form extended parallel sheets two molecules thick, called planar bilayers. The individual molecules lie perpendicular to the sheets, with hydrophilic groups on the outside in aqueous solution and on the inside in nonpolar media. When segments of planar bilayers fold back on themselves, unilamellar vesicles may form where the spherical hydrophobic bilayer shell separates an inner aqueous compartment from the external aqueous environment.



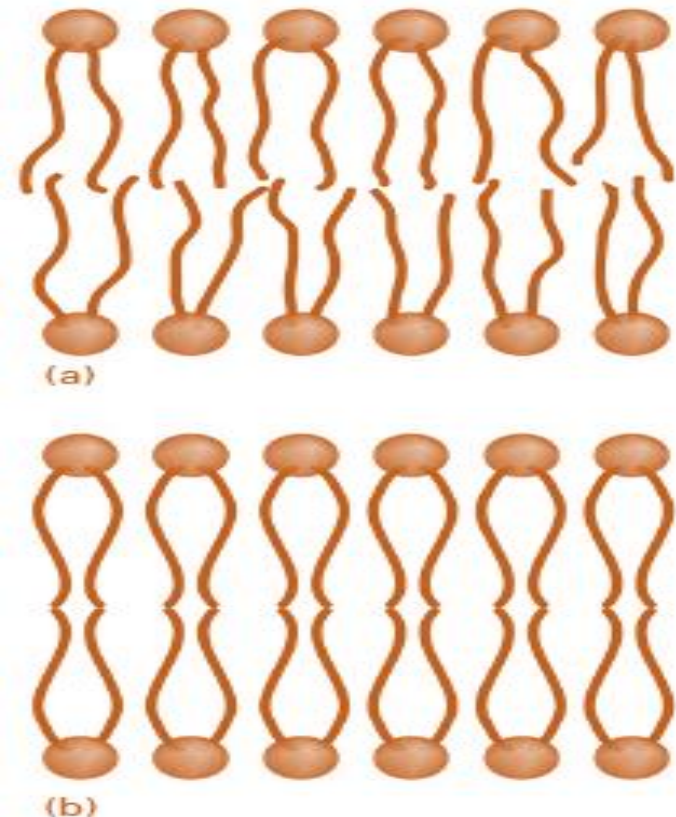
9 Phosphatidyl choline

Bilayers show a close resemblance to biological membranes, and are often a useful model on which to base investigations of biological structures. However, actual membranes are highly sophisticated structures. The basic structural element of a membrane is a phospholipid, such as phosphatidyl choline (9), which contains long hydrocarbon chains (typically in the range C_{14} – C_{24}) and a variety of polar groups, such as $-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_3^+$. The hydrophobic chains stack together to form an extensive layer about 5 nm across. The lipid molecules form layers instead of micelles because the hydrocarbon chains are too bulky to allow packing into nearly spherical clusters.

The bilayer is a highly mobile structure, as shown by EPR studies with spin-labelled phospholipids (*Impact 114.2*). Not only are the hydrocarbon chains ceaselessly twisting and turning in the region between the polar groups, but the phospholipid and cholesterol molecules migrate over the surface. It is better to think of the membrane as a viscous fluid rather than a permanent structure, with a viscosity about 100 times that of water. In common with diffusional behaviour in general (Section 20.8), the average distance a phospholipid molecule diffuses is proportional to the square-root of the time; more precisely, for a molecule confined to a two-dimensional plane, the average distance travelled in a time t is equal to $(4Dt)^{1/2}$. Typically, a phospholipid molecule migrates through about 1 μm in about 1 min.

All lipid bilayers undergo a transition from a state of high to low chain mobility at a temperature that depends on the structure of the lipid. To visualize the transition, we consider what happens to a membrane as we lower its temperature (Fig. 18.26). There is sufficient energy available at normal temperatures for limited bond rotation to occur and the flexible chains writhe. However, the membrane is still highly organized in the sense that the bilayer structure does not come apart and the system is best described as a liquid crystal. At lower temperatures, the amplitudes of the writhing motion decrease until a specific temperature is reached at which motion is largely frozen. The membrane is said to exist as a gel. Biological membranes exist as liquid crystals at physiological temperatures.

Fig. 18.26 A depiction of the variation with temperature of the flexibility of hydrocarbon chains in a lipid bilayer. (a) At physiological temperature, the bilayer exists as a liquid crystal, in which some order exists but the chains writhe. (b) At a specific temperature, the chains are largely frozen and the bilayer is said to exist as a gel.



Phase transitions in membranes are often observed as ‘melting’ from gel to liquid crystal by differential scanning calorimetry (*Impact 12.1*). The data show relations between the structure of the lipid and the melting temperature. For example, the melting temperature increases with the length of the hydrophobic chain of the lipid. This correlation is reasonable, as we expect longer chains to be held together more strongly by hydrophobic interactions than shorter chains. It follows that stabilization of the gel phase in membranes of lipids with long chains results in relatively high melting temperatures. On the other hand, any structural elements that prevent alignment of the hydrophobic chains in the gel phase lead to low melting temperatures. Indeed, lipids containing unsaturated chains, those containing some C=C bonds, form membranes with lower melting temperatures than those formed from lipids with fully saturated chains, those consisting of C–C bonds only.

Interspersed among the phospholipids of biological membranes are sterols, such as cholesterol (10), which is largely hydrophobic but does contain a hydrophilic –OH group. Sterols, which are present in different proportions in different types of cells, prevent the hydrophobic chains of lipids from ‘freezing’ into a gel and, by disrupting the packing of the chains, spread the melting point of the membrane over a range of temperatures.

Self-assembled monolayers

Molecular self-assembly can be used as the basis for manipulation of surfaces on the nanometre scale. Of current interest are self-assembled monolayers (SAMs), ordered molecular aggregates that form a single layer of material on a surface. To understand the formation of SAMs, consider exposing molecules such as alkyl thiols RSH, where R represents an alkyl chain, to an Au(0) surface. The thiols react with the surface, forming $\text{RS}^- \text{Au(I)}$ adducts:



If R is a sufficiently long chain, van der Waals interactions between the adsorbed RS units lead to the formation of a highly ordered monolayer on the surface, as shown in Fig. 18.27. It is observed that the Gibbs energy of formation of SAMs increases with the length of the alkyl chain, with each methylene group contributing 400–4000 J mol⁻¹ to the overall Gibbs energy of formation.

A self-assembled monolayer alters the properties of the surface. For example, a hydrophilic surface may be rendered hydrophobic once covered with a SAM. Furthermore, attaching functional groups to the exposed ends of the alkyl groups may impart specific chemical reactivity or ligand-binding properties to the surface, leading to applications in chemical (or biochemical) sensors and reactors.

