SURFACTANTS

1. Introduction

Surface active agents (usually referred to as surfactants) are amphipathic molecules consisting of a nonpolar hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain containing 8–18 carbon atoms, which is attached to a polar or ionic portion (hydrophilic). The hydrophilic portion can, therefore, be nonionic, ionic or zwitterionic, accompanied by counter ions in the last two cases. The hydrocarbon chain interacts weakly with the water molecules in an aqueous environment, whereas the polar or ionic head group interacts strongly with water molecules via dipole or ion-dipole interactions. It is this strong interaction with the water molecules that renders the surfactant soluble in water. However, the cooperative action of dispersion and hydrogen bonding between the water molecules tends to squeeze the hydrocarbon chain out of the water and hence these chains are referred to as hydrophobic. The balance between hydrophobic and hydrophilic part of the molecule gives these systems their special properties, eg, accumulation at various interfaces and association in solution (to form micelles).

The driving force for surfactant adsorption is the lowering of the free energy of the phase boundary. The interfacial free energy per unit area is the amount of work required to expand the interface. This interfacial free energy, referred to as surface or interfacial tension, γ, is given in $\mathrm{mJm^{-2}}$ or $\mathrm{mNm^{-1}}$. Adsorption of surfactant molecules at the interface lowers γ and the higher the surfactant adsorption (ie, the more dense the layer is) the larger the reduction in γ. The degree of surfactant adsorption at the interface depends on surfactant structure and the nature of the two phases that meet the interface (1,2).

Surface active agents also aggregate in solution forming micelles. The driving force micelle formation (or micellization) is the reduction of contact between the hydrocarbon chain and water, thereby reducing the free energy of the system. In the micelle, the surfactant hydrophobic groups are directed towards the interior of the aggregate and the polar head groups are directed towards the solvent. These micelles are in dynamic equilibrium and the rate of exchange between a surfactant molecule and the micelle may vary by orders of magnitude, depending on the structure of the surfactant molecule.

Surfactants find application in almost every chemical industry of which the following may be worth mentioning: detergents, paints, dyestuffs, cosmetics, pharmaceuticals, agrochemicals, fibers, plastics, etc. Moreover, surfactants play a major role in the oil industry, for example, in enhanced and tertiary oil recovery. They are also occasionally used for environmental protection, eg, in oil slick dispersants. Therefore, a fundamental understanding of the physical chemistry of surface active agents, their unusual properties and their phase behavior is essential for most industrial chemists. In addition, an understanding of the basic phenomena involved in the application of surfactants, such as in the preparation of emulsions and suspensions and their subsequent stabilization, in microemulsions, in wetting spreading and adhesion, etc, is of vital importance in arriving at the right composition and control of the system involved (1,2). This is particularly the case with many formulations in the chemical industry mentioned above.

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It should be stated that commercially produced surfactants are not pure chemicals, and within each chemical type there can be tremendous variation. This can be understood, since surfactants are prepared from various feedstocks, namely petrochemicals, natural vegetable oils and natural animal fats. It is important to realize that in every case the hydrophobic group exists as a mixture of chains of different lengths. The same applied to the polar head group, for example, in the case of polyethylene oxide (the major component of nonionic surfactants) which consists of a distribution of ethylene oxide units. Hence, products that may be given the same generic name could vary a great deal in their properties and the formulation chemist should bear this in mind when choosing a surfactant from a particular manufacturer. It is advisable to obtain as much information as possible from the manufacturer about the properties of the surfactant chosen such as its suitability for the job, its batch to batch variation, its toxicity, etc. The manufacturer usually has more information on the surfactant than that printed in the data sheet, and in most cases such information is given on request.

2. Properties of Solutions

The physical properties of surface active agents differ from those of smaller or nonamphipathic molecules in one major aspect, namely the abrupt changes in their properties above a critical concentration (1,2). This is illustrated in Fig. 1 in which a number of physical properties (osmotic pressure, turbidity, solubilization, magnetic resonance, surface tension, equivalent conductivity and self diffusion) are plotted as a function of concentration for an ionic surfactant (1,2).

At low concentrations, most properties are similar to those of a simple electrolyte. One notable exception is the surface tension which decreases rapidly with increase in surfactant concentration. However, all the properties (interfacial and bulk) show an abrupt change of a particular concentration, that is consistent with the fact that at and above this concentration, surface active ions or molecules in solution associate to form larger units. These associated units are called micelles (self-assembled structures) and the first formed aggregates are generally approximately spherical in shape. A schematic representation of a spherical micelle is given in Fig. 2.

The concentration at which this association phenomenon occurs is known as the critical micelle concentration (cmc). Each surfactant molecules has a characteristic cmc value at a given temperature and electrolyte concentration. The most common technique for measuring the cmc is surface tension, γ, which shows break at the cmc, after which γ remains virtually constant with further increase in concentration. However, other techniques such as self diffusion measurements, nmr and fluorescence spectroscopy can be applied. A compilation of cmc values has been given in 1971 by Mukerjee and Mysels, which is clearly not an up-to-date text, but is an extremely valuable reference. As an illustration, the cmc values of a number of surface active agents are given in Table 1, to show some of the general trends (1,2). Within any class of surface active agent, the cmc decreases with increase in chain length of the hydrophobic portion (alkyl group). As a general rule, the cmc decreases by a factor of 2 for ionics (without added salt) and by a factor of 3 for nonionics on adding one methylene group to the alkyl chain. With nonionic surfactants, increasing the length of the hydrophilic group (polyethylene oxide) causes an increase in cmc.

In general, nonionic surfactants have lower cmc values than their corresponding ionic surfactants of the same alkyl chain length. Incorporation of a phenyl group in the alkyl group increases its hydrophobicity to a much smaller extent than increasing its chain length with the same number of carbon atoms. The valency of the counterion in ionic surfactants has a significant effect on the cmc. For example, increasing the valency of the counter ion from 1 to 2 causes a reduction of the cmc by roughly a factor of 4.

The cmc is, to a first approximation, independent of temperature. This is illustrated in Fig. 3 which shows the variation of cmc of SDS with temperature. The cmc varies in a non-monotonic way by ca 10–20% over a wide temperature range. The shallow minimum around 25°C can be compared with a similar minimum in the solubility of hydrocarbon in water (1). However, nonionic surfactants of the ethoxylate type show a monotonic decrease (1) of cmc with increase of temperature (Fig. 3).

The effect of addition of cosolutes, eg, electrolytes and nonelectrolytes, on the cmc can be very striking. For example addition of 1:1 electrolyte to a solution of anionic surfactant gives a dramatic lowering of the cmc, which may amount to an order of magnitude. The effect is moderate for short-chain surfactants, but is much larger for long-chain ones. At high electrolyte concentrations, the reduction in cmc with increase in number of carbon atoms in the alkyl chain is much stronger than without added electrolyte. This rate of decrease at high electrolyte concentrations is comparable to that of nonionics. The effect of added electrolyte also depends on the valency of the added counterions. In contrast, for nonionics, addition of electrolytes causes only small variation in the cmc.

Nonelectrolytes such as alcohols can also cause a decrease in the cmc (1,2). The alcohols are less polar than water and are distributed between the bulk solution and the micelles. The more preference they have for the micelles, the more they stabilize them. A longer alkyl chain leads to a less favorable location in water and more favorable location in the micelles.

The presence of micelles can account for many of the unusual properties of solutions of surface active agents. For example, it can account for the near constant surface tension value, above the cmc (See Fig. 1). It also accounts for the reduction in molar conductance of the surface active agent solution above the cmc, which is consistent with the reduction in mobility of the micelles as a result of counterion association. The presence of micelles also accounts for the rapid increase in light scattering or turbidity above the cmc.

The presence of micelles was originally suggested by McBain (2) who suggested that below the cmc most of the surfactant molecules are unassociated, whereas in the isotropic solutions immediately above the cmc, micelles and surfactant ions (molecules) are thought to co-exist, the concentration of the latter changing very slightly as more surfactant is dissolved. However, the self association of an amphiphile occurs in a stepwise manner with one monomer added to the aggregate at a time. For a long chain amphiphile, the association is strongly cooperative up to a certain micelle size where counteracting factors became increasingly important. Typically the micelles have a closely spherical shape in a rather wide concentration range above the cmc. Originally, it was suggested by Adam (2) and Hartley (2) that micelles are spherical in shape and have the following properties: (*1*) the association unit is spherical with a radius approximately equal to the length of the hydrocarbon chain; (*2*) the micelle contains about 50–100 monomeric units - aggregation number generally increases with increase in alkyl chain length; (*3*) with ionic surfactants, most counterions are bound to the micelle surface, thus significantly reducing the mobility from the value to be expected from a micelle with noncounterion bonding; (*4*) micellization occurs over a narrow concentration range as a result of the high association number of surfactant micelles; (*5*) the interior of the surfactant micelle has essentially the properties of a liquid hydrocarbon. This is confirmed by the high mobility of the alkyl chains and the ability of the micelles to solubilize many water insoluble organic molecules, eg, dyes and agrochemicals.

To a first approximation, micelles can, over a wide concentration range above the cmc, be viewed as microscopic liquid hydrocarbon droplets covered with polar head groups, which interact strongly with water molecules. It appears that the radius of the micelle core constituted of the alkyl chains is close to the extended length of the alkyl chain, ie, in the range 1.5030 nm. The driving force for micelle formation is the elimination of the contact between the alkyl chains and water. The larger a spherical micelle, then the more efficient this is, since the volume-to-area ratio increases. It should be noted that the surfactant molecules in the micelles are not all extended. Only one molecule needs to be extended to satisfy the criterion that the radius of the micelle core is close to the extended length of the alkyl chain. The majority of surfactant molecules are in a disordered state. In other words, the interior of the micelle is close to that of the corresponding alkane in a neat liquid oil. This explains the large solubilization capacity of the micelle towards a broad range of nonpolar and weakly polar substances.

At the surface of the micelle associated counter ions (in the region of 50–80% of the surfactant ions) are present. However, simple inorganic counterions are very loosely associated with the micelle. The counterions are very mobile (see below) and there is no specific complex formed with a definite counterion-head group distance. In other words, the counterions are associated by long-range electrostatic interactions.

A useful concept for characterizing micelle geometry is the critical packing parameter, CPP. The aggregation number N is the ratio between the micellar core volume, V_{mic}, and the volume of one chain, v,

$$N = \frac{V_{mic}}{v} = \frac{(4/3)\pi R_{mic}^3}{v} \tag{1}$$

where R_{mic} is the radius of the micelle.

The aggregation number, N, is also equal to the ratio of the area of a micelle, A_{mic}, to the cross sectional area, a, of one surfactant molecule,

$$N = \frac{A_{mic}}{a} = \frac{4\pi R_{mic}^2}{a} \tag{2}$$

Combining equations 1 and 2,

$$\frac{v}{R_{mic}a} = \frac{1}{3} \tag{3}$$

Since R_{mic} cannot exceed the extended length of a surfactant alkyl chain, l_{max},

$$l_{max} = 1.5 + 1.265n_c \tag{4}$$

This means that for a spherical micelle,

$$\frac{v}{l_{max}\,a} \leq \frac{1}{3} \tag{5}$$

The ratio $v/(l_{max}\ a)$ is denoted as the critical packing parameter (CPP).

Although, the spherical micelle model accounts for many of the physical properties of solutions of surfactants, a number of phenomena remain unexplained, without considering other shapes. For example, McBain (2) suggested the presence of two types of micelles, spherical and lamellar in order to account for the drop in molar conductance of surfactant solutions. The lamellar micelles are neutral and hence they account for the reduction in the conductance. Later, Harkins and co-workers (2) used McBain's model of lamellar micelles to interpret his x-ray results in soap solutions. Moreover, many modern techniques such as light scattering and neutron scattering indicate that in many systems the micelles are not spherical. For example, Debye and Anacker (24) proposed a cylindrical micelle to explain that light scattering results on hexadecyltrimethyl ammonium bromide in water. Evidence for disc-shaped micelles have also been obtained under certain conditions. A schematic representation of the spherical, lamellar and rod-shaped micelles, suggested by McBain, Hartley and Debye is given in Fig. 4.

2.1. Solubility-Temperature Relationship for Surfactants. Many ionic surfactants show dramatic temperature-dependent solubility. This is illustrated in Fig. 5 for sodium decyl benzene sulfonate. The solubility may be very low at low temperatures and then increases by orders of magnitude in a relatively narrow temperature range. This phenomenon is generally denoted as the Krafft phenomenon with the temperature for the onset of increasing solubility being known as the Krafft temperature. The latter may vary dramatically with subtle changes in the surfactant chemical structure. In general, the Krafft temperature increases rapidly as the alkyl chain length of the surfactant increases. It also depends on the head group and counterion. Addition of electrolytes causes an increase in the Krafft temperature.

The solubility–temperature relationship for nonionic surfactants shows a different behavior from ionic surfactants. This is illustrated in Fig. 6 which shows the phase diagram of $C_{12}EO_6$. The nonionic surfactant forms a clear solution (micellar phase) up to a certain temperature (that depends on concentration) above which the solution becomes cloudy. This critical temperature, denoted as the cloud point (CP) of the solution, decrease with increase in surfactant concentration reaching a minimum at a given concentration (denoted as the lower consolute temperature) above which the CP increases with further increase in surfactant concentration. Above the cloud point curve the system separates into two layers (water + solution). Below the cloud-point curve, several liquid crystalline phases can be identified as the surfactant concentration exceeds a certain limit. Three different liquid crystalline phases can be identified, namely the hexagonal, the cubic, and lamellar phases. A schematic picture of the structure of these three phases is shown in Fig. 7.

3. Thermodynamics of Micellization

The process of micellization is one of the most important characteristics of surfactant solution and hence it is essential to understand its mechanism (the driving force for micelle formation). This requires analysis of the dynamics of the process (ie, the kinetic aspects) as well as the equilibrium aspects whereby the laws of thermodynamics may be applied to obtain the free energy, enthalpy, and entropy of micellization.

3.1. Kinetic Aspects. Micellization is a dynamic phenomenon in which n monomeric surfactant molecules associate to form a micelle S_n, ie,

$$nS \Leftrightarrow S_n \tag{6}$$

Hartley (2) envisaged a dynamic equilibrium whereby surface active agent molecules are constantly leaving the micelles where other molecules from solution enter the micelles. The same applies to the counterions with ionic surfactants, which can exchange between the micelle surface and bulk solution.

Experimental investigation using fast kinetic methods such as stop flow, temperature and pressure jumps, and ultrasonic relaxation measurements have shown that there are two relaxation processes for micellar equilibrium (2) characterized by relaxation times τ_1 and τ_2. The first relaxation time, τ_1, is of the order of 10^{-7} s (10^{-8} to 10^{-3} s) and represents the life-time of a surface active molecule in a micelle, ie, it represents the association and dissociation rate for a single molecule entering and leaving the micelle, which may be represented by the equation,

$$S + S_{n-1} \Leftrightarrow S_n \tag{7}$$

where K^+ and K^- represent the association and dissociation rate respectively for a single molecule entering or leaving the micelle.

The slower relaxation time τ_2 corresponds to a relatively slow process, namely the micellization - dissolution process represented by equation 1. The value of τ_2 is of the order of milleseconds (10^{-3}–1 s) and hence can be conveniently measured by stopped flow methods. The fast relaxation time τ_1 can be measured using various techniques depending on its range. For example, τ_1 values in the range of 10^{-8}–10^{-7} s are accessible to ultrasonic absorption methods, whereas τ_1 in the range of 10^{-5}–10^{-3} s can be measured by pressure jump methods. The value of τ_1 depends on surfactant concentration, chain length and temperature. τ_1 increases with increase of chain length of surfactants, ie, the residence time increases with increase of chain length.

The above discussion emphasizes the dynamic nature of micelles and it is important to realize that these molecules are in continuous motion and that there is a constant interchange between micelles and solution. The dynamic nature also applies to the counterions which exchange rapidly with life times in the range 10^{-9}–10^{-8} s. Furthermore, the counterions appear to be laterally mobile and not to be associated with (single) specific groups on the micelle surfaces (2).

3.2. Equilibrium Aspects. Two general approaches have been employed in tackling the problem of micelle formation. The first and most simple approach treats micelles as a single phase, and this is referred to as the phase separation model. In this model, micelle formation is considered as a phase separation phenomenon and the cmc is then the saturation concentration of the amphiphile in the monomeric state, whereas the micelles constitute the separated pseudophase. Above the cmc, a phase equilibrium exists with a constant activity of the surfactant in the micellar phase. The Krafft point is viewed as the temperature at which solid hydrated surfactant, micelles, and a solution saturated with undissociated surfactant molecules are in equilibrium at a given pressure.

In the second approach, micelles and single surfactant molecules or ions are considered to be in association–dissociation equilibrium. In its simplest form, a single equilibrium constant is used to treat the process represented by equation 1. The cmc is merely a concentration range above which any added surfactant appears in solution in a micellar form. Since the solubility of the associated surfactant is much greater than that of the monomeric surfactant, the solubility of the surfactant as a whole will not increase markedly with temperature until it reaches the cmc region. Thus, in the mass action approach, the Krafft point represents the temperature at which the surfactant solubility equals the cmc.

3.3. Phase Separation Model. Consider an anionic surfactant, in which n surfactant anions, S^-, and n counterions M^+ associate to form a micelle, ie,

$$nS^- + nM^+ \rightleftharpoons S_n \tag{8}$$

The micelle is simply a charged aggregate of surfactant ions plus an equivalent number of counterions in the surrounding atmosphere and is treated as a separate phase.

The chemical potential of the surfactant in the micellar state is assumed to be constant, at any given temperature, and this may be adopted as the standard chemical potential, $\mu_m{}^\circ$, by analogy to a pure liquid or a pure solid. Considering the equilibrium between micelles and monomer, then,

$$\mu_m^\circ = \mu_1^\circ + RT \ln a \tag{9}$$

where μ_1 is the standard chemical potential of the surfactant monomer and a_1 is its activity which is equal to $f_1\,x_1$, where f_1 is the activity coefficient and x_1 the mole fraction. Therefore, the standard free energy of micellization per mol of monomer, ΔG_m°, is given by,

$$\Delta G_m^\circ = \mu_m^\circ - \mu_1^\circ = RT\ln a_1 - RT\ln x_1 \tag{10}$$

where f_1 is taken as unity (a reasonable value in very dilute solution). The cmc may be identified with x_1 so that

$$\Delta G_m^\circ = RT\ln[cmc] \tag{11}$$

In equation 10, the cmc is expressed as a mole fraction, which is equal to $C/(55.5 + C)$, where C is the concentration of surfactant in mole dm^{-3}, ie,

$$\Delta G_m^\circ = RT\ln C - RT\ln(55.5 + C) \tag{12}$$

It should be stated that ΔG° should be calculated using the cmc expressed as a mole fraction as indicated by equation 12. However, most cmc quoted in the literature are given in mole dm^{-3} and, in many cases of ΔG° values have been quoted, when the cmc was simply expressed in mol dm^{-3}. Strictly speaking, this is incorrect, since ΔG° should be based on x_1 rather than on C. The value of ΔG°, when the cmc is expressed in mol dm^{-3} is substantially different from the ΔG° value when the cmc is expressed in mole fraction. For example, dodecyl hexaoxyethylene glycol, the quoted cmc value is 8.7×10^{-5} mol dm^{-3} at 25°C. Therefore,

$$\Delta G^\circ = RT\ln\frac{8.7 \times 10^{-5}}{55.5 + 8.7 \times 10^{-5}} = -33.1\,\mathrm{KJ\,mol^{-1}} \tag{13}$$

when the mole fraction scale is used. On the other hand,

$$\Delta G^\circ = RT\ln 8.7 \times 10^{-5} = -23.2\,\mathrm{KJ\,mol^{-1}} \tag{14}$$

when the molarity scale is used.

The phase separation model has been questioned for two main reasons. First, according to this model a clear discontinuity in the physical property of a surfactant solution, such as surface tension, turbidity, etc should be observed at the cmc. This is not always found experimentally and the cmc is not a sharp break point. Second, if two phases actually exist at the cmc, then equating the chemical potential of the surfactant molecule in the two phases would imply that the activity of the surfactant in the aqueous phase would be constant above the cmc. If this was the case, the surface tension of a surfactant solution should remain constant above the cmc. However, careful measurements have shown that the surface tension of a surfactant solution decreases slowly above the cmc, particularly when using purified surfactants.

3.4. Mass Action Model. This model assumes a dissociation–association equilibrium between surfactant monomers and micelles and an equilibrium constant can be calculated. For a nonionic surfactant, where charge effects are absent, this equilibrium is simply represented by equation 1 which assumes a single equilibrium. In this case, the equilibrium constant K_m is given by the equation,

$$K_m = \frac{[S_n]}{[S]^n} \tag{15}$$

The standard free energy per monomer is then given by,

$$-\Delta G^{\circ}_m = -\frac{\Delta G}{n} = \frac{RT}{n} \ln K_m = \frac{RT}{n} \ln [S_n] - RT \ln [S] \tag{16}$$

For many micellar systems, $n > 50$ and, therefore, the first term on the right hand side of equation 16 may be neglected, resulting in the following expression for ΔG°_m,

$$\Delta G^{\circ}_m = RT \ln [S] = RT \ln [cmc] \tag{17}$$

which is identical to the equation derived using the phase separation model.

The mass action model allows a simple extension to be made to the case of ionic surfactants, in which micelles attract a substantial proportion of counterions, into an attached layer. For a micelle made of n-surfactant ions (where n-p) charges are associated with counterions, ie, having a net charge of p units and degree of dissociation p/n, the following equilibrium may be established (for an anionic surfactant with Na$^+$ counterions).

$$n\,S^- + (n-p)Na^+ \Leftrightarrow S_n^{p^-} \tag{18}$$

$$K_m = \frac{[S_n^{p^-}]}{[S^-]^n [Na^+]^{(n-p)}} \tag{19}$$

A convenient solution for relating ΔG_m to [cmc] was given by Phillips (2) who arrived at the following expression,

$$\Delta G^{\circ}_m = \{2 - (p/n)\} RT \ln [cmc] \tag{20}$$

For many ionic surfactants, the degree of dissociation (p/n) is ~ 0.2 so that,

$$\Delta G^{\circ}_m = 1.8\, RT \ln [cmc] \tag{21}$$

Comparison with equation 17 clearly shows that for similar ΔG_m, the [cmc] is about two orders of magnitude higher for ionic surfactants when compared with nonionic surfactant of the same alkyl chain length (see Table 1).

In the presence of excess added electrolyte, with mole fraction x, the free energy of micellization is given by the expression,

$$\Delta G^{\circ}_m = RT \ln [cmc] + \{1 - (p/n)\} \ln x \tag{22}$$

Equation 22 shows that as x increases, the [cmc] decreases.

It is clear from equation 20 that as p → 0, ie, when most charges are associated with counterions,

$$\Delta G_m^{\circ} = 2RT\ln[cmc] \tag{23}$$

whereas when $p \sim n$, ie, the counterions are bound to micelles,

$$\Delta G_m^{\circ} = RT\ln[cmc] \tag{24}$$

which is the same equation for nonionic surfactants.

Although the mass action approach could account for a number of experimental results such as small change in the properties around the cmc, it has not escaped criticism. For example, the assumption that surfactants exist in solution in only two forms, namely single ions and micelles of uniform size is debatable. Analysis of various experimental results has shown that micelles have a size distribution which is narrow and concentration dependent. Thus, the assumption of a single aggregation number is an oversimplification and in reality there is a micellar size distribution. This can be analyzed using the multiple equilibrium model which can be best formulated as a stepwise aggregation (2),

$$S_1 + S_1 \rightleftharpoons S_2 \tag{25}$$

$$S_2 + S_1 \rightleftharpoons S_3 \tag{26}$$

$$S_{n-1} + S_1 \rightleftharpoons S_n \tag{27}$$

As noted in particular in the analysis of kinetic data (1,2) there are aggregates over a wide range of aggregation numbers, from dimers and well beyond the most stable micelles. However, for surfactants with not too high cmc, the size distribution curve has a very deep minimum, the least stable aggregates being present in concentrations many orders of magnitude below those of the most abundant micelles. For surfactants with predominantly spherical micelles, the polydispersity is low and there is then a particularly preferred micellar size.

3.5. Enthalpy and Entropy of Micellization. The enthalpy of micellization can be calculated from the variation of cmc with temperature. This follows from,

$$-\Delta H^{\circ} = RT^2 \frac{dln[cmc]}{dT} \tag{28}$$

The entropy of micellization can then be calculated from the relationship between ΔG° and ΔH°, ie,

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{29}$$

Therefore ΔH° may be calculated from the surface tension–log C plots at various temperatures. Unfortunately, the errors in locating the cmc (which in many cases is not a sharp point) leads to a large error in the value of ΔH°. A more accurate and direct method of obtaining ΔH° is microcalorimetry. As an illustration, the thermodynamic parameters, ΔG°, ΔH°, and $T\Delta S^\circ$ for octylhexaoxyethylene glycol monoether (C_8E_6) are given in Table 2.

It can be seen from Table 2 that ΔG° is large and negative. However, ΔH° is positive, indicating that the process is endothermic. In addition, $T\Delta S^\circ$ is large and positive which implies that in the micellization process there is a net increase in entropy. This positive enthalpy and entropy points to a different driving force for micellization from that encountered in many aggregation processes.

The influence of alkyl chain length of the surfactant on the free energy, enthalpy, and entropy of micellization, was demonstrated by Rosen (2) who listed these parameters as a function of alkyl chain length for sulphoxide surfactants. The results are given in Table 3 it can be seen that the standard free energy of micellization becomes increasingly negative as the chain length increases. This is to be expected since the cmc decreases with increase of the alkyl chain length. However, ΔH° becomes less positive and $T\Delta S$ becomes more positive with increase in chain length of the surfactant. Thus, the large negative free energy of micellization is made up of a small positive enthalpy (which decreases slightly with increase of the chain length of the surfactant) and a large positive entropy term $T\Delta S^\circ$, which becomes more positive as the chain is lengthened. These results can be accounted for in terms of the hydrophobic effect.

3.6. Driving Force for Micelle Formation. Until recently, the formation of micelles was regarded primarily as an interfacial energy process, analogous to the process of coalescence of oil droplets in an aqueous medium. If this was the case, micelle formation would be a highly exothermic process, as the interfacial free energy has a large enthalpy component. As mentioned above, experimental results have clearly shown that micelle formation involves only a small enthalpy change and is often endothermic. The negative free energy of micellization is the result of a large positive entropy. This led to the conclusion that micelle formation must be predominantly entropy driven process. Two main sources of entropy may have been suggested. The first is related to the so called “hydrophobic effect”. The latter effect was first established from a consideration of the free energy enthalpy and entropy of transfer of hydrocarbon from water to a liquid hydrocarbon. To account for the large positive entropy of transfer several authors (1,2) suggest that the water molecules around a hydrocarbon chain are ordered, forming “clusters” or “icebergs”. On transfer of an alkane from water to a liquid hydrocarbon, these clusters are broken thus releasing water molecules which now have a higher entropy. This accounts for the large entropy of transfer of an alkane from water to a hydrocarbon medium. This effect is also reflected in the much higher heat capacity change on transfer, ΔC_p°, when compared with the heat capacity in the gas phase, C_p°.

The above effect is also operative on transfer of surfactant monomer to a micelle, during the micellization process. The surfactant monomers will also contain “structured” water around their hydrocarbon chain. On transfer of such monomers to a micelle, these water molecules are released and they have a higher entropy.

The second source of entropy increase on micellization may arise from the increase in flexibility of the hydrocarbon chains on their transfer from an aqueous to a hydrocarbon medium (2). The orientations and bendings of an organic chain are likely to be more restricted in an aqueous phase compared to an organic phase.

It should be mentioned that with ionic and zwitterionic surfactants, an additional entropy contribution, associated with the ionic head groups, must be considered. Upon partial neutralization of the ionic charge by the counterions when aggregation occurs, water molecules are released. This will be associated with an entropy increase which should be added to the entropy increase resulting from the hydrophobic effect mentioned above. However, the relative contribution of the two effects is difficult to asssess in a quantitative manner.

4. Adsorption of Surfactants

4.1. At the Air/Liquid and Liquid/Liquid Interfaces. As mentioned in the general introduction, surfactants play a major role in the formulation of most chemical products. In the first place they are used for stabilization of emulsions and microemulsions. Second, surfactants are added in emulsifiable concentrates for their spontaneous dispersion on dilution.

In all the above mentioned phenomenon, the surfactant needs to accummulate at the interface, a process that is generally described as adsorption. The simplest interface is that of the air/liquid and in this case, the surfactant will adsorb with the hydrophilic group pointing towards the polar liquid (water) leaving the hydrocarbon chain pointing towards the air. This process results in lowering of the surface tension tension γ. Typically, surfactants show a gradual reduction in γ, till the cmc is reached above which the surface tension remains virtually constant. Hydrocarbon surfactants of the ionic, nonionic or Zwitteronic ionic type lower the surface tension to limiting values reaching 30–40 mNm^{-1} depending on the nature of the surfactant. Lower values may be achieved using fluorocarbon surfactants, typically of the order of 20 mNm^{-1}. It is, therefore, essential to understand the adsorption and conformation of surfactants at the air/liquid interface.

With emulsifiable concentrates, emulsions, and microemulsion, the surfactant adsorbs at the oil/water interface, with the hydrophilic head group immersed in the aqueous phase, leaving the hydrocarbon chain in the oil phase. Again, the mechanism of stabilization of emulsions and microemulsions depends on the adsorption and orientation of the surfactant molecules at the liquid/liquid interface.

Before describing surfactant adsorption at the air/liquid (A/L) and liquid/liquid (L/L) interface it is essential to define the interface. The surface of a liquid is the boundary between two bulk phases, namely liquid and air (or the liquid vapor). Similarly an interface between two immiscible liquids (oil and water) may be defined providing a dividing line is introduced since the interfacial region is not a layer that is one molecule thick, but usually have a thickness δ with properties that are different from the two bulk phases α and β (1). However, Gibbs (2) introduced the concept of a mathematical dividing plane Z_σ in the interfacial region (Fig. 8).

In this model the two bulk phases α and β are assumed to have uniform thermodynamic properties up to Z_σ. This picture applies for both the air/liquid and liquid/liquid interface (with A/L interfaces, one of the phase is air saturated with the vapor of the liquid).

Using the Gibbs model, it is possible to obtain a definition of the surface or interfacial tension γ, starting from the Gibbs-Deuhem equation 2, ie,

$$dG^\sigma = -S^\sigma\, dT + Ad\gamma + \Sigma n_i d\,\mu_i \tag{30}$$

where G^σ is the surface free energy, S^σ is the entropy, A is the area of the interface, n_i is the number of moles of component i with chemical potential μ_i at the interface. At constant temperature and composition of the interface (ie, in absence of any adsorption)

$$\gamma = \left(\frac{\partial G^\sigma}{\partial A}\right)_{T,n_i} \tag{31}$$

It is obvious from equation 31, that for a stable interface γ should be positive. In other words, the free energy should increase if the area of the interface increases, otherwise the interface will become convoluted, increasing the interfacial area, until the liquid evaporates (for A/L Case) or the two “immiscible” phases dissolved in each other (for the L/L case).

It is clear from equation 31, that surface or interfacial tension, ie, the force per unit length tangentially to the surface measured in units of mNm^{-1}, is dimensionally equivalent to an energy per unit area measured in mJm^{-2}. For this reason, it has been stated that the excess surface free energy is identical to the surface tension, but this is true only for a single component system, ie, a pure liquid (where the total adsorption is zero).

There are generally two approaches for treating surfactant adsorption at the A/L and L/L interface. The first approach, adopted by Gibbs, treats adsorption as an equilibrium phenomenon whereby the second law of thermodynamics may be applied using surface quantities. The second approach, referred to as the equation of state approach, treats the surfactant film as a two-dimensional layer with a surface pressure Π that may be related the surface excess Γ (amount of surfactant adsorbed per unit area). Below, only the Gibbs approach will be considered.

Gibbs (2) derived a thermodynamic relationship between the surface or interfacial tension γ and the surface excess Γ (adsorption per unit area). The starting point of this equation is the Gibbs-Deuhem equation (eq. 30). At constant temperature, but in the presence of adsorption, equation 30 reduces to,

$$d\gamma = \sum \frac{n_i^\sigma}{A} d\mu_i = -\sum \Gamma_i d\mu_i \tag{32}$$

where $\Gamma_i = n_i^\sigma / A$ is the number of moles of component i and adsorbed per unit area.

Equation 32 is the general form for the Gibbs adsorption isotherm. The simplest case of this isotherm is a system of two component in which the solute (2) is the surface active component, ie, it is adsorbed at the surface of the solvent (1). For such a case, equation 32 may be written as,

$$-d\gamma = \Gamma_1^\sigma d\,\mu_1 + \Gamma_2^\sigma d\,\mu_2 \tag{33}$$

and if the Gibbs dividing surface is used, $\Gamma_1 = 0$ and,

$$-d\gamma = \Gamma_{1,2}^\sigma d\,\mu_2 \tag{34}$$

where $\Gamma_{2,1}^\sigma$ is the relative adsorption of (2) with respect to (1). Since,

$$\mu_2 = \overset{\circ}{\mu_2} + RT \ln a_2^L \tag{35}$$

or,

$$d\,\mu_2 = RT\,dln\,a_2^L \tag{36}$$

then,

$$-d\gamma = \Gamma_{2,1}^\sigma RT\,dln\,a_2^L \tag{37}$$

or

$$\Gamma_{2,1}^\sigma = -\frac{1}{RT}\left(\frac{d\gamma}{dln\,a_2^L}\right) \tag{38}$$

where a_2^L is the activity of the surfactant in bulk solution that is equal to C_2f_2 or x_2f_2, where C_2 is the concentration of the surfactant in moles dm^{-3} and x_2 is its mole fraction.

Equation 38 allows one to obtain the surface excess (abbreviated as Γ_2) from the variation of surface or interfacial tension with surfactant concentration. Note that $a_2 \sim C_2$ since in dilute solutions $f_2 \sim 1$. This approximation is valid since most surfactants have low cmc (usually less than 10^{-3} mol dm^{-3}) but adsorption is complete at or just below the cmc.

The surface excess Γ_2 can be calculated from the linear portion of the $\gamma - \log C_2$ curves before the cmc. Such $\gamma - \log C$ curves are illustrated in Fig. 9 for the air/water and *o/w* interfaces; $[C_{SAA}]$ denotes the concentration of surface active agent in bulk solution. It can be seen that for the *A/W* interface γ decreases from the value for water (72 mNm^{-1} at 20°C) reaching about 25–30 mNm^{-1} near the cmc. This is clearly schematic since the actual values depend on the surfactant nature. For the *o/w* case, γ decreases from a value of about 50 mNm^{-1} (for a pure hydrocarbon–water interface) to $\sim$ 1–5 mNm^{-1} near the cmc (again depending on the nature of the surfactant).

As mentioned above Γ_2 can be calculated from the slope of the linear position of the curves shown in Fig. 9 just before the cmc is reached. From Γ_2, the area per surfactant ion or molecule can be calculated since,

$$Area/molecule = \frac{1}{\Gamma_2 N_{av}} \tag{39}$$

where N_{av} is the Avogadro's constant. Determining the area per surfactant molecule is very useful since it gives information on surfactant orientation at the interface. For example, for ionic surfactants such as sodium dodecyl sulfate, the area per surfactant is determined by the area occupied by the alkyl chain and head group if these molecules lie flat at the interface, whereas for vertical orientation, the area per surfactant ion is determined by that occupied by the charged head group, which at low electrolyte concentration will be in the region of 0.40 nm^2. Such area is larger than the geometrical area occupied by a sulfate group, as a result of the lateral repulsion between the head group. On addition of electrolytes, this lateral repulsion is reduced and the area/surfactant ion for vertical orientation will be lower than 0.4 nm^2 (reaching in some case 0.2 nm^2). On the other hard, if the molecules lie flat at the interface the area per surfactant ion will be considerably higher than 0.4 nm^2.

Another important point can be made from the $\gamma - \log C$ curves. At concentration just before the break point, one has the condition of constant slope, which indicates that saturation adsorption has been reached.

$$\left(\frac{\partial \gamma}{\partial \ln a_2}\right)_{p,T} = \text{constant} \tag{40}$$

Just above the break point,

$$\left(\frac{\partial \gamma}{\partial \ln a_2}\right)_{p,T} = 0 \tag{41}$$

indicating the constancy of γ with $\log C$ above the cmc. Integration of equation 30 gives,

$$\gamma = \text{constant}\, x \ln a_2 \tag{42}$$

Since γ is constant in this region, then a_2 must remain constant. This means that addition of surfactant molecules, above the cmc must result in association to form units (micellar) with low activity.

As mentioned before, the hydrophilic head group may be unionized, eg, alcohols or poly(ethylene oxide) alkane or alkyl phenol compounds, weakly ionized such as carboxylic acids or strongly ionized such as sulfates, sulfonates and quaternary ammonium salts. The adsorption of these different surfactants at the air/water and oil/water interface depends on the nature of the head group. With nonionic surfactants, repulsion between the head groups is small and these surfactants are usually strongly adsorbed at the surface of water from very dilute solutions. As mentioned before, nonionic surfactants have much lower cmc values when compared with ionic surfactants with the same alkyl chain length. Typically, the cmc is in the region of 10^{-5}–10^{-4} mol dm^{-3}. Such nonionic surfactants form closely packed adsorbed layers at concentrations lower than their cmc values. The activity coefficient of such surfactants is close to unity and is only slightly affected by addition of moderate amounts of electrolytes (or change in the pH of the solution). Thus, nonionic surfactant adsorption is the simplest case since the solutions can be represented by a two component system and the adsorption can be accurately calculated using equation 9.

With ionic surfactants, on the other hand, the adsorption process is relatively more complicated since one has to consider the repulsion between the head groups and the effect of presence of any indifferent electrolyte. Moreover, the Gibbs adsorption equation has to be solved taking into account the surfactant ions, the counterion and any indifferent electrolyte ions present. For a strong surfactant electrolyte such as an $Na^+ R^-$

$$\Gamma_2 = \frac{1}{2RT}\frac{\partial\gamma}{\partial \ln a^+} \tag{43}$$

The factor of 2 in equation 13 arises because both surfactant ion and counter ion must be adsorbed to maintain neutrality, and $d\gamma/d\ln a^+$ is twice as large as for an unionized surfactant.

If a nonadsorbed electrolyte, such as NaCl, is present in large excess, then any increase in concentration of Na^+R^- produces a negligible increase in Na^+ ion concentration and therefore $d\mu_{Na}$ becomes negligible. Moreover, $d\mu_{Cl}$ is also negligible, so that the Gibbs adsorption equation reduces to,

$$\Gamma_2 = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial lnC_{NaR}}\right) \tag{44}$$

ie, it becomes identical to that for a nonionic surfactant.

The above discussion, clearly illustrates that for calculation of Γ_2 from the $\gamma - \log C$ curve one has to consider the nature of the surfactant and the composition of the medium. For nonionic surfactants the Gibbs adsorption equation 38 can be used directly. For ionic surfactant, in absence of electrolytes the right hand side of the equation 38 should be divided by 2 to account for surfactant dissociation. This factor disappears in the presence of a high concentration of an indifferent electrolyte.

4.2. At the Solid/Liquid Interface. The use of surfactants (ionic, nonionic and zwitterionic) and polymers to control the stability behavior of suspensions is of considerable technological importance. Surfactants and polymers are used in the formulation of dyestuffs, paints, paper coatings, agrochemicals, pharmaceuticals, ceramics, printing inks, etc. They are particularly robust form of stabilization which is useful at high disperse volume fractions and high electrolyte concentrations, as well as under extreme conditions of high temperature, pressure, and flow. In particular, surfactants and polymers are essential for the stabilization of suspensions in nonaqueous media, where electrostatic stabilization is less successful.

The key to understanding how surfactants function as stabilizers is to know their adsorption and conformation at the solid/liquid interface.

Surfactant adsorption may be described in terms of simple interaction parameters, namely chain-solvent, chain-surface, and surface solvent. However, in some cases these interaction parameters may involve ill-defined forces, such as hydrophobic bonding, solvation forces, and chemisorption. In addition, the adsorption of ionic surfactants involves electrostatic forces particularly with polar surfaces containing ionogenic groups. For that reason, the adsorption of ionic and nonionic surfactants is treated separately. The surfaces (substrates) can be also hydrophobic or hydrophilic and these may be treated separately.

The adsorption of ionic surfactants on hydrophobic surfaces such as carbon black, polymer surfaces and ceramics (silicon carbide or silicon nitride) is governed by hydrophobic interaction between the alkyl chain of the surfactant and the hydrophobic surface. In this case, electrostatic interaction will play a relatively smaller role. However, if the surfactant head group is of the same sign of charge as that on the substrate surface, electrostatic repulsion may oppose adsorption. In contrast, if the head groups are of opposite sign to the surface, adsorption may be enhanced. Since the adsorption depends on the magnitude of the hydrophobic bonding free energy, the amount of surfactant adsorbed increases directly with increase in the alkyl chain length in accordance with Traube's rule.

The adsorption of ionic surfactants on hydrophobic surfaces may be represented by the Stern-Langgmuir isotherm. Consider a substrate containing N_s sites (mol m^{-2}) on which Γ moles m^{-2} of surfactant ions are adsorbed. The surface coverage θ is (Γ/N_s) and the fraction of uncovered surface is $(1 - \theta)$.

$$\frac{\theta}{1-\theta} = \frac{C}{55.5}\exp\left(-\frac{\Delta G^{\circ}_{ads}}{RT}\right) \tag{45}$$

Equation 45 applies only at low surface coverage ($\theta < 0.1$) where lateral interaction between the surfactant ions can be neglected.

At high surface coverage ($\theta > 0.1$) one should take the lateral interaction between the chains into account, by introducing a constant A, eg, using the Frumkin-Fowler-Guggenheim equation,

$$\frac{\theta}{(1-\theta)}\exp(A\theta) = \frac{C}{55.5}\exp\left(-\frac{\Delta G^{\circ}_{ads}}{RT}\right) \tag{46}$$

Various authors have used the Stern-Langmuir equation in a simple form to describe the adsorption of surfactant ions on mineral surfaces,

$$\Gamma = 2r\,C\exp\left(-\frac{\Delta G^{\circ}_{ads}}{RT}\right) \tag{47}$$

Various contributions to the adsorption free energy may be envisaged. To a first approximation, these contributions may be considered to be additive. In the first instance, ΔG_{ads} may be taken to consist of two main contributions, ie,

$$\Delta G_{ads} = \Delta G_{elec} + \Delta G_{spec} \tag{48}$$

where ΔG_{elec} accounts for any electrical interactions and ΔG_{spec} is a specific adsorption term which contains all contributions to the adsorption free energy that are dependent on the “specific” (non-electrical) nature of the system (2). Several authors subdivided ΔG_{spec} into supposedly separate independent interactions (2), eg,

$$\Delta G_{spec} = \Delta G_{cc} + \Delta G_{cs} + \Delta G_{hs} + \ldots\ldots\ldots \tag{49}$$

where ΔG_{cc} is a term that accounts for the cohesive chain–chain interaction between the hydrophobic moieties of the adsorbed ions, ΔG_{cs} is the term for chain/substrate interaction whereas ΔG_{hs} is a term for the head group/substrate interaction. Several other contributions to ΔG_{spec} may be envisaged, eg, ion-dipole, ion-induced dipole, or dipole-induced dipole interactions.

Since there is no rigorous theory that can predict adsorption isotherms, the most suitable method to investigate adsorption of surfactants is to determine the adsorption isotherm. Measurement of surfactant adsorption is fairly straightforward. A known mass m (g) of the particles (substrate) with known specific surface area A_s ($m^2\ g^{-1}$) is equilibrated at constant temperature with surfactant solution with initial concentration C_1. The suspension is kept stirred for sufficient time to reach equilibrium. The particles are then removed from the suspension by centrifugation and the equilibrium concentration C_2 is determined using a suitable analytical method. The amount of adsorption Γ (mole m^{-2}) is calculated as follows,

$$\Gamma = \frac{(C_1 - C_2)}{m A_s} \tag{50}$$

The adsorption isotherm is represented by plotting Γ versus C_2. A range of surfactant concentrations should be used to cover the whole adsorption process, ie, from the initial values low to the plateau values. To obtain accurate results, the solid should have a high surface area (usually $> 1\ \mathrm{m}^2$).

Several examples may be quoted from the literature to illustrate the adsorption of surfactant ions on solid surfaces. For a model hydrophobic surface, carbon black has been chosen (2). Figure 10 shows typical results for the adsorption of sodium dodecyl sulfate (SDS) on two carbon black surfaces, namely Spheron 6 untreated and of the Graphon (graphitized) which also describes the effect of surface treatment. The adsorption of SDS on untreated Spheron 6 tends to show a maximum that is removed on washing. This suggests the removal of impurities from the carbon black which becomes extractable at high surfactant concentration. The plateau adsorption value is $\sim 2 \times 10^{-6}$ mol m^{-2} (~ 2 μ mole m^{-2}). This plateau value is reached at ~ 8 m mole dm^{-3} SDS, ie, close to the cmc of the surfactant in the bulk solution. The area per surfactant ion in this case is $\sim$ 0.7 nm^2. Graphitization (Graphon) removes the hydrophilic ionizable groups (eg, – C=O or –COOH), producing a surface that is more hydrophobic. The same occurs by heating Spheron 6 to 2700°C. This leads to a different adsorption isotherm (Fig. 10) showing a step (inflection point) at a surfactant concentration in the region of ~ 6 m mole dm^{-3}. The first plateau value is ~ 2.3 μ mole m^{-2}

whereas the second plateau value (that occurs at the cmc of the surfactant) is ~ 4 μ mole m^{-2}. It is likely in this case that the surfactant ions adopt different orientations at the first and second plateaus. In the first plateau region, a more "flat" orientation (alkyl chains adsorbing parallel to the surface) is obtained whereas at the second plateau vertical orientation is more favorable, with the polar head groups being directed towards the solution phase. Addition of electrolyte (10^{-1} mole dm^{-3} NaCl) enhance the surfactant adsorption. This increase is due to the reduction of lateral repulsion between the sulfate head groups and this enhances the adsorption.

The adsorption of ionic surfactants on hydrophobic polar surfaces resembles that for carbon black. For example, Saleeb and Kitchener (2) found similar limiting area for cetyltrimethyl ammonium bromide on Graphon and polystyrene (~ 0.4 nm^2). As with carbon black, the area per molecule depends on the nature and amount of added electrolyte. This can be accounted for in terms of reduction of head group repulsion and/or counter ion binging.

Surfactant adsorption close to the cmc may appear Langmuirian, although this does not automatically imply a simple orientation. For example, rearrangement from horizontal to vertical orientation or electrostatic interaction and counter ion binding may be masked by simple adsorption isotherms. It is essential, therefore, to combine the adsorption isotherms with other techniques such as microcalorimetry and various spectroscopic methods to obtain a full picture on surfactant adsorption.

The adsorption of ionic surfactants on polar surfaces that contain ionizable groups may show characteristic features due to additional interaction between the head group and substrate and/or possible chain–chain interaction. This is best illustrated by the results of adsorption of sodium dodecyl sulfonate (SDSe) on alumina at $pH = 7.2$ obtained by Fuersetenau (2) and shown in Fig. 11. At the pH value, the alumina is positively charged (the isoelectric point of alumina is at pH ~ 9) and the counter ions are Cl^- from the added supporting electrolyte. In Fig. 11, the saturation adsorption Γ_1 is plotted versus equilibrium surfactant concentration C_1 in logarithmic scales. The figure also shows the results of zeta potential (ζ) measurements (which are a measure of the magnitude sign of charge on the surface). Both adsorption and zeta potential results show three distinct regions. The first region which shows a gradual increase of adsorption with increase in concentration, with virtually no change in the value of the zeta potential corresponds to an ion-exchange process. In other words, the surfactant ions simply exchange with the counter ions (Cl^-) of the supporting electrolyte in the electrical double layer. At a critical surfactant concentration, the adsorption increases dramatically with further increase in surfactant concentration (region II). In this region, the positive zeta potential gradually decrease, reaching a zero value (charge neutralization) after which a negative value is obtained which increases rapidly with increase in surfactant concentration. The rapid increase in region II was explained in terms of "hemi-micelle formation" that was originally postulated by Gaudin and Fuerestenau. In other words, at a critical surfactant concentration (to be denoted the cmc of "hemi-micelle formation" or better the critical aggregation concentration CAC), the hydrophobic moieties of the adsorbed surfactant chains are "squeezed out" from the aqueous solution by forming two-dimensional aggregates on the adsorbent surface. This is analogous to the process of micellization in bulk solution. However, the CAC is lower than the cmc, indicating that the substrate promotes surfactant aggregation. At a certain surfactant concentration in the hemi-micellization process, the isoelectric point is exceeded and, thereafter, the adsorption is hindered by the electrostatic repulsion between the hemi-micelles micelles and hence the slope of the adsorption isotherm is reduced (region III).

Several types of nonionic surfactants exist, depending on the nature of the polar (hydrophilic) group. The most common type is that based on a poly(oxyethylene) glycol group, ie, $(CH_2CH_2O)_nOH$ (where n can vary from as little as 2 units to as high as 100 or more units) linked either to an alkyl (C_xH_{2x+1}) or alkyl phenyl $(C_xH_{2x+1}{-}C_6H_4{-})$ group. These surfactants may be abbreviated as C_xE_n or $C_{x\varphi}E_n$ (where C refers to the number of C atoms in the alkyl chain, φ denotes C_6H_4 and E denotes ethylene oxide). These ethoxylated surfactants are characterized by a relatively large head group compared to the alkyl chain (when $n > 4$). However, there are nonionic surfactants with small head group such as amine oxides $(-N \rightarrow O)$ head group, phosphate oxide $(-P \rightarrow O)$ or sulfinyl-alkanol $(-SO{-}(CH_2)_n{-}OH)$. Most adsorption isotherms in the literature are based on the ethoxylated type surfactants.

The adsorption isotherm of nonionic surfactants are in many cases Langmuirian, like those of most other highly surface active solutes adsorbing from dilute solutions and adsorption is generally reversible. However, several other adsorption types are produced and those are illustrated in Fig. 12. The steps in the isotherm may be explained in terms of the various adsorbate-adsorbate, adsorbate-adsorbent and adsorbate-solvent interactions. These orientations are schematically illustrated in Fig. 13. In the first stage of adsorption (denoted by I in Figs. 12 and 13), surfactant–surfactant interaction is negligible (low coverage) and adsorption occurs mainly by van der Waals interaction. On a hydrophobic surface, the interaction is dominated by the hydrophobic portion of the surfactant molecule. This is mostly the case with agrochemicals which have hydrophobic surfaces. However, if the chemical is hydrophilic in nature, the interaction will be dominated by the EO chain. The approach to monolayer saturation with the molecules lying flat is accompanied by a gradual decrease in the slope of the adsorption isotherm (region II in Fig. 12). Increase in the size of the surfactant molecule, eg, increasing the length of the alkyl or EO chain will decrease adsorption (when expressed in moles per unit area). On the other hand, increasing temperature will increase adsorption as a result of desolvation of the EO chains, thus reducing their size. Moreover, increasing temperature reduces the solubility of the nonionic surfactant and this enhances adsorption.

The subsequent stages of adsorption (region III and IV) are determined by surfactant–surfactant interaction, although surfactant–surface interaction initially determines adsorption beyond stage II. This interaction depends on the nature of the surface and the hydrophilic-lipophilic balance of the surfactant molecule (HLB). For a hydrophobic surface, adsorption occurs via the alkyl group of the surfactant. For a given EO chain, the adsorption will increase with increase in the alkyl chain length. On the other hand, for a given alkyl chain length, adsorption increases with decrease of the PEO chain length. As the surfactant concentration approaches the cmc, there is a tendency for aggregation of the alkyl groups. This will cause vertical orientation of the surfactant molecules (stage IV). The will compress the head group and for an EO chain this will result in a less coiled more extended conformation. The larger the surfactant alkyl chain the greater will be the cohesive forces and hence the smaller the cross sectional area. This may explain why saturation adsorption increases with increasing alkyl chain length. The interaction occurring in the adsorption layer during the fourth and subsequent stages of adsorption are similar to those that occur in bulk solution. In this case aggregate units, as shown in Fig. 13 V (hemi-micelles or micelles) may be formed.

5. General Classification of Surface Active Agents

A simple classification of surfactants based on the nature of the hydrophilic group is commonly used. Three main classes may be distinguished, namely anionic, cationic, and amphoteric. A useful technical reference is McCutcheon (3), which is produced annually to update the list of available surfactants. A recent text by van Os and co-workers (4) listing the physicochemical properties of selected anionic, cationic, and nonionic surfactants has been published by Elsevier. Another useful text is the *Handbook of Surfactants* by Porter (5). It should be mentioned also that a fourth class of surfactants, usually referred to as polymeric surfactants, has been used for many years for preparation of emulsions and suspensions and their stabilization.

5.1. Anionic Surfactants.

These are the most widely used class of surfactants in industrial applications (5). This is due to their relatively low cost of manufacture and they are used practically in every type of detergent. For optimum detergency the hydrophobic chain is a linear alkyl group with a chain length in the region of 12–16 C atoms. Linear chains are preferred since they are more effective and more degradable than the branched chains. The most commonly used hydrophilic groups are carboxylates, sulfates, sulfonates and phosphates. A general formula may be ascribed to anionic surfactants as follows:

Carboxylates: $C_nH_{2n+1}\ COO^-\ X$
Sulfates: $C_nH_{2n+1}\ OSO_3{}^-\ X$
Sulfonates: $C_nH_{2n+1}\ SO_3{}^-\ X$
Phosphates: $C_nH_{2n+1}\ OPO(OH)O^-\ X$

n is the range 8–16 atoms and the counterion X is usually Na^+.

Several other anionic surfactants are commercially available such as sulfosuccinates, isethionates and taurates and these are sometimes used for special applications.

Carboxylates. These are perhaps the earliest known surfactants, since they constitute the earliest soaps, eg, sodium or potassium stearate, $C_{17}H_{35}COONa$, sodium myristate, $C_{14}H_{29}COONa$. The alkyl group may contain unsaturated portions, eg, sodium oleate, which contains one double bond in the C_{17} alkyl chain. Most commercial soaps will be a mixture of fatty acids obtained from tallow, coconut oil, palm oil, etc. The main attraction of these simple soaps is their low cost, their ready biodegradability, and low toxicity. Their main disadvantages is their ready precipitation in water containing bivalent ions such as Ca^{2+} and Mg^{2+}. To avoid their precipitation in hard water, the carboxylates are modified by introducing some hydrophilic chains, eg, ethoxy carboxylates with the general structure $RO(CH_2CH_2O)_nCH_2COO^-$, ester carboxylates containing hydroxyl or multi COOH groups, sarcosinates which contain an amide group with the general structure $RCON(R')COO^-$.

The addition of the ethoxylated groups results in increased water solubility and enhanced chemical stability (no hydrolysis). The modified ether carboxylates are also more compatible with electrolytes. They are also compatible with other nonionic, amphoteric, and sometimes even cationic surfactants. The ester carboxylates are very soluble in water, but they suffer from the problem of hydrolysis. The sarcosinates are not very soluble in acid or neutral solutions, but they are quite soluble in alkaline media. They are compatible with other anionics, nonionics and cationics. The phosphate esters have very interesting properties since they are intermediate between ethoxylated nonionics and sulfated derivatives. They have good compatibility with inorganic builders and they can be good emulsifiers. A specific salt of a fatty acid is lithium 12-hydroxystearic acid that forms the major constituent of greases.

Sulfates. These are the largest and most important class of synthetic surfactants, which were produced by reaction of an alcohol with sulfuric acid, ie, they are esters of sulfuric acid. In practice sulfuric acid is seldom used and chlorosulfonic or sulfur dioxide/air mixtures are the most common methods of sulfating the alcohol. However, due to their chemical instability (hydrolyzing to the alcohol, particularly in acid solutions), they are now overtaken by the sulfonates which are chemically stable.

The properties of sulfate surfactants depend on the nature of the alkyl chain and the sulfate group. The alkali metal salts show good solubility in water, but they tend to be affected by the presence of electrolytes. The most common sulfate surfactant is sodium dodecyl sulfate (abbreviated as SDS and sometimes referred to as sodium lauryl sulfate) which is used extensively both for fundamental studies and many applications in industry. At room temperature ($\sim 25°C$) this surfactant is quite soluble and 30% aqueous solutions are fairly fluid (low viscosity). However, below 25°C, the surfactant may separate out as a soft paste as the temperature falls below its Krafft point (the temperature above which the surfactant shows a rapid increase in solubility with further increase of temperature). The latter depends on the distribution of chain lengths in the alkyl chain, the wider the distribution the lower the Krafft temperature. Thus, by controlling this distribution one may achieve a Krafft temperature of $\sim$10°C. As the surfactant concentration is increased to 30–40% (depending on the distribution of chain length in the alkyl group), the viscosity of the solution increases very rapidly and may produce a gel. The critical micelle concentration (cmc) of SDS (the concentration above which the properties of the solution show abrupt changes) is 8×10^{-3} mol dm^{-3} (0.24%).

As with the carboxylates, the sulfate surfactants are also chemically modified to change their properties. The most common modification is to introduce some ethylene oxide units in the chain, usually referred to as alcohol ether sulfates. For example, sodium dodecyl 3-mole ether sulfate which is essentially dodecyl alcohol reacted with 3 moles EO, then sulfated and neutralized by NaOH. The presence of PEO confers improved solubility when compared with the straight alcohol sulfates. In addition, the surfactant becomes more compatible with electrolytes in aqueous solution. The ether sulfates are also more chemically stable than the alcohol sulfates. The cmc of the ether sulfates is also lower than the corresponding surfactant without the EO units.

Sulfonates. With sulfonates, the sulfur atom is directly attached to the carbon atom of the alkyl group and this gives the molecule stability against hydrolysis, when compared with the sulfates (whereby the sulfur atom is indirectly linked to the carbon of the hydrophobe via an oxygen atom). The alkyl aryl sulfonates are the most common type of these surfactants (for example, sodium alkyl benzene sulfonate) and these are usually prepared by reaction of sulfuric acid with alkyl aryl hydrocarbons, eg, dodecyl benzene. A special class of sulfonate surfactants are the naphthalene and alkyl naphthalene sulfonates which are commonly used as dispersants.

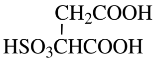
As with the sulfates, some chemical modification is used by introducing ethylene oxide units, eg, sodium nonyl phenol 2-mole ethoxylate ethane sulfonate $C_9H_{19}C_6H_4(OCH_2CH_2)_2SO_3^-Na^+$.

The paraffin sulfonates are produced by sulfo-oxidation of normal linear paraffins with sulfur dioxide and oxygen and catalyzed with ultraviolet or gamma radiation. The resulting alkane sulfonic acid is neutralized with NaOH. These surfactants have excellent water solubility and biodegradability. They are also compatible with many aqueous ions.

The linear alkyl benzene sulfonates (LABS) are manufactured from alkyl benzene and the alkyl chain length can vary from C_8 to C_{15} and their properties are mainly influenced by the average molecular weight and the spread of carbon number of the alkyl side chain. The cmc of sodium dodecyl benzene sulfonate is 5×10^{-3} mol dm^{-3} (0.18%). The main disadvantages of LABS is their effect on the skin and hence they cannot be used in personal care formulations.

Another class of sulfonates is the α-olefin sulfonates which are prepared by reacting linear α-olefin with sulfur trioxide, typically yielding a mixture of alkene sulfonates (60–70%), 3- and 4-hydroxyalkane sulfonates ($\sim$ 30%) and some disulfonates and other species. The two main α-olefin fractions used as starting material are C_{12}–C_{16} and C_{16}–C_{18}.

A special class of sulfonates are sulfosuccinates which are esters of sulfosuccinic acid,

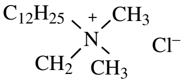


$$\begin{array}{l} \quad\ \ CH_2COOH \\ \quad\ \ | \\ HSO_3CHCOOH \end{array}$$

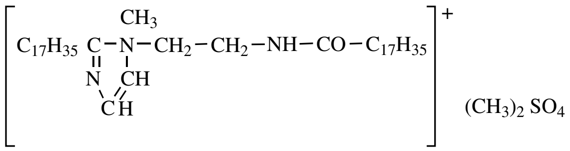
Both mono and diesters are produced. A widely used diester in many formulations is sodium di(2-ethylhexyl)sulfosuccinate (that is sold commercially under the trade name Aerosol OT). The diesters are soluble both in water and in many organic solvents. They are particularly useful for preparation of water-in-oil (W/O) microemulsions.

Phosphate Containing Anionic Surfactants. Both alkyl phosphates and alkyl ether phosphates are made by treating the fatty alcohol or alcohol ethoxylates with a phophorylating agent, usually phosphorous pentoxide, P_4O_{10}. The reaction yields a mixture of mono- and di-esters of phosphoric acid. The ratio of the two esters is determined by the ratio of the reactants and the amount of water present in the reaction mixture. The physicochemical properties of the alkyl phosphate surfactants depend on the ratio of the esters. Phosphate surfactants are used in the metal working industry due to their anticorrosive properties.

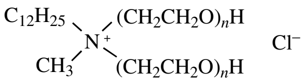
5.2. Cationic Surfactants. The most common cationic surfactants are the quaternary ammonium compounds with the general formula $R'R''R'''R''''N^+X^-$, where X^- is usually chloride ion and R represents alkyl groups. A common class of cationics is the alkyl trimethyl ammonium chloride, where R contains 8–18 C atoms, eg, dodecyl trimethyl ammonium chloride, $C_{12}H_{25}(CH_3)_3NCl$. Another widely used cationic surfactant class is that containing two long chain alkyl group, ie, dialkyl dimethyl ammonium chloride, with the alkyl groups having a chain length of 8–18 C atoms. These dialkyl surfactants are less soluble in water than the monoalkyl quaternary compounds, but they are commonly used in detergents as fabric softeners. A widely used cationic surfactant is alkyl dimethyl benzyl ammonium chloride (sometimes referred to as benzalkonium chloride and widely used as bactericide), having the structure,



Imidazolines can also form quaternaries, the most common product being the ditallow derivative quaternized with dimethyl sulfate,



Cationic surfactants can also be modified by incorporating polyethylene oxide chains, eg, dodecyl methyl polyethylene oxide ammonium chloride having the structure,



Cationic surfactants are generally water soluble when there is only one long alkyl group. They are generally compatible with most inorganic ions and hard water, but they are incompatible with metasilicates and highly condensed phosphates. They are laos incompatible with protein-like materials. Cationics are generally stable to pH changes, both acid and alkaline. They are incompatible with most anionic surfactants, but they are compatible with nonionics. These cationic surfactants are insoluble in hydrocarbon oils. In contrast, cationics with two or more long alkyl chains are soluble in hydrocarbon solvents, but they become only dispersible in water (sometimes forming bilayer vesicle type structures). They are generally chemically stable and can tolerate electrolytes. The cmc of cationic surfactants is close to that of anionics with the same alkyl chain length.

The prime use of cationic surfactants is their tendency to adsorb at negatively charged surfaces, eg, anticorrosive agents for steel, flotation collectors for mineral ores, dispersants for inorganic pigments, antistatic agents for plastics, antistatic agents and fabric softeners, hair conditioners, anticaking agent for fertilizers and as bactericides.

5.3. Amphoteric (Zwitterionic) Surfactants. These are surfactants containing both cationic and anionic groups (10). The most common amphoterics are the *N*-alkyl betaines which are derivatives of trimethyl glycine $(CH_3)_3NCH_2COOH$ (that was described as betaine). An example of betaine surfactant is lauryl amido propyl dimethyl betaine $C_{12}H_{25}CON(CH_3)_2CH_2COOH$. These alkyl betaines are sometimes described as alkyl dimethyl glycinates.

The main characteristics of amphoteric surfactants is their dependence on the pH of the solution in which they are dissolved. In acid pH solutions, the molecule acquires a positive charge and it behaves like a cationic, whereas in alkaline pH solutions, they become negatively charged and behave like an anionic. A specific pH can be defined at which both ionic groups show equal ionization (the isoelectric point of the molecule). This can be described by the following scheme,

$$\begin{array}{lclcl} N^+\ldots COOH & \leftrightarrow & N^+\ldots COO^- & \leftrightarrow & NH\ldots COO^- \\ \text{acid pH} < 3 & & \text{isoelectric} & & \text{pH} > 6 \text{ alkaline} \end{array}$$

Amphoteric surfactants are sometimes referred to as zwitterionic molecules. They are soluble in water, but the solubility shows a minimum at the isoelectric point. Amphoterics show excellent compatibility with other surfactants, forming mixed micelles. They are chemically stable both in acids and alkalies. The surface activity of amphoterics vary widely and it depends on the distance between the charged groups and they show a maximum in surface activity at the isoelectric point.

Another class of amphoteric are the *N*-alkyl amino propionates having the structure $R{-}NHCH_2CH_2COOH$. The NH group is reactive and can react with another acid molecule (eg, acrylic) to form an amino dipropionate $R{-}N(CH_2CH_2COOH)_2$. Alkyl imidazoline-based product can also be produced by reacting alkyl imidozoline with a chloro acid. However, the imidazoline ring breaks down during the formation of the amphoteric.

The change in charge with pH of amphoteric surfactants affects their properties, such as wetting, detergency, foaming, etc. At the isoelectric point, the properties of amphoterics resemble those of nonionics very closely. Below and above the iep, the properties shift towards those of cationic and anionic surfactants respectively. Zwitterionic surfactants have excellent dermatological properties. They also cause low eye irritation and they are frequently used in shampoos and other personal care products (cosmetics).

5.4. Nonionic Surfactants. The most common nonionic surfactants are those based on ethylene oxide, referred to as ethoxylated surfactants. Several classes can be distinguished: alcohol ethoxylates, alkyl phenol ethoxylates, fatty acid ethoxylates, monoalkaolamide ethoxylates, sorbitan ester ethoxylates, fatty amine ethoxylates and ethylene oxide–propylene oxide copolymers (sometimes referred to as polymeric surfactants).

Another important class of nonionics are the multihydroxy products such as glycol esters, glycerol (and polyglycerol) esters, glucosides (and polyglucosides) and sucrose esters. Amine oxides and sulfinyl surfactants represent nonionics with a small head group.

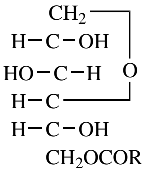
Alcohol Ethoxylates. These are generally produced by ethoxylation of a fatty chain alcohol such as dodecanol. Several generic names are given to this class of surfactants such as ethoxylated fatty alcohols, alkyl polyoxyethylene glycol, monoalkyl polyethylene oxide glycol ethers, etc. A typical example is dodecyl hexaoxyethylene glycol monoether with the chemical formula $C_{12}H_{25}(OCH_2CH_2O)_6OH$ (sometimes abbreviated as $C_{12}E_6$). In practice, the starting alcohol will have a distribution of alkyl chain lengths and the resulting ethoxylate will have a distribution of ethylene oxide chain length. Thus the numbers listed in the literature refer to average numbers.

The cmc of nonionic surfactants is about two orders of magnitude lower than the corresponding anionics with the same alkyl chain length. The solubility of the alcohol ethoxylates depend both on the alkyl chain length and the number of ethylene oxide units in the molecule. Molecules with an average alkyl chain length of 12 C atoms and containing more than 5 EO units are usually soluble in water at room temperature. However, as the temperature of the solution is gradually raised, the solution becomes cloudy (as a result of dehydration of the PEO chain) and the temperature at which this occurs is referred to as the cloud point (CP) of the surfactant. At a given alkyl chain length, the CP increases with increase in the EO chain of the molecule. The CP changes with change of concentration of the surfactant solution and the trade literature usually quotes the CP of a 1% solution. The CP is also affected by the presence of electrolyte in the aqueous solution. Most electrolytes lower the CP of a nonionic surfactant solution. Nonionics tend to have maximum surface activity near to the cloud point. The CP of most nonionics increases markedly on the addition of small quantities of anionic surfactants. The surface tension of alcohol ethoxylate solutions decreases with decrease in the EO units of the chain. The viscosity of a nonionic surfactant solution increases gradually with increase in its concentration, but at a critical concentration (which depends on the alkyl and EO chain length) the viscosity show a rapid increase and ultimately a gel-like structure appears. This results from the formation of liquid crystalline structure of the hexagonal type. In many cases, the viscosity reaches a maximum after which it shows a decrease due to the formation of other structures (eg, lamellar phases).

Alkyl Phenol Ethoxylates. These are prepared by reaction of ethylene oxide with the appropriate alkyl phenol. The most common surfactants of this type are those based on nonyl phenol. These surfactants are cheap to produce, but they suffer from the problem of biodegradability and potential toxicity (the by product of degradation is nonyl phenol which has considerable toxicity). Inspite of these problems, nonyl phenol ethoxylates are still used in many industrial properties, due to their advantageous properties, such as their solubility both in aqueous and nonaqueous media, their good emulsification and dispersion properties, etc.

Fatty Acid Ethoxylates. These are produced by reaction of ethylene oxide with a fatty acid or a polyglycol and they have the general formula $RCOO{-}(CH_2CH_2O)_nH$. When a polyglycol is used, a mixture of mono- and di-ester ($RCOO{-}(CH_2CH_2O)_n{-}OCOR$) is produced. These surfactants are generally soluble in water provided there is enough EO units and the alkyl chain length of the acid is not too long. The mono-esters are much more soluble in water than the di-esters. In the latter case, a longer EO chain is required to render the molecule soluble. The surfactants are compatible with aqueous ions, provided there is not much unreacted acid. However, these surfactants undergo hydrolysis in highly alkaline solutions.

Sorbitan Esters and their Ethoxylated Derivatives (Spans and Tweens). The fatty acid esters of sorbitan (generally referred to as Spans, an Atlas commercial trade name) and their ethoxylated derivatives (generally referred to as Tweens) are perhaps one of the most commonly used nonionics. They were first commercialized by Atlas in the U.S. which has been purchased by ICI. The sorbitan esters are produced by reaction of sorbitol with a fatty acid at a high temperature (> 200°C). The sorbitol dehydrates to 1,4- sorbitan and then esterification takes place. If one mole of fatty acid is reacted with one mole of sorbitol, one obtains a mono-ester (some di-ester is also produced as a byproduct). Thus, sorbitan mono-ester has the following general formula,



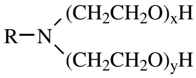
The free OH groups in the molecule can be esterified, producing di- and tri-esters. Several products are available depending on the nature of the alkyl group of the acid and whether the product is a mono-, di- or tri-ester. Some examples are: sorbitan monolaurate, Span 20; sorbitan monopalmitate, Span 40; sorbitan monostearate, Span 60; sorbitan mono-oleate, Span 80; sorbitan tristearate, Span 65; and sorbitan trioleate, Span 85.

The ethoxylated derivatives of Spans (Tweens) are produced by reaction of ethylene oxide on any hydroxyl group remaining on the sorbitan ester group. Alternatively, the sorbitol is first ethoxylated and then esterified. However, the final product has different surfactant properties to the Tweens. Some examples of Tween surfactants are: polyoxyethylene (20) sorbitan monolaurate, Tween 20; polyoxyethylene (20) sorbitan monopalmitate, Tween 40; polyoxyethylene (20) sorbitan monostearate, Tween 60; polyoxyethylene (20) sorbitan mono-oleate, Tween 80; and polyoxyethylene (20) sorbitan tristearate, Tween 65; and polyoxyethylene (20) sorbitan tri-oleate, Tween 85.

The sorbitan esters are insoluble in water, but soluble in most organic solvents (low HLB number surfactants). The ethoxylated products are generally soluble in water and they have relatively high HLB numbers. One of the main advantages of the sorbitan esters and their ethoxylated derivatives is their approval as food additives. They are also widely used in cosmetics and some pharmaceutical preparations.

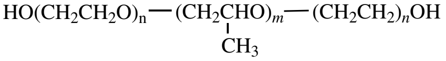
Ethoxylated Fats and Oils. A number of natural fats and oils have been ethoxylated, eg, lanolin (wool fat) and castor oil ethoxylates. These products are useful for application in pharmaceutical products, eg, as solubilizers.

Amine Ethoxylates. These are prepared by addition of ethylene oxide to primary or secondary fatty amines. With primary amines both hydrogen atoms on the amine group react with ethylene oxide and therefore the resulting surfactant has the structure:



The above surfactants acquire a cationic character if the EO units are small in number and if the pH is low. However, at high EO levels and neutral pH they behave very similarly to nonionics. At low EO content, the surfactants are not soluble in water, but become soluble in an acid solution. At high pH, the amine ethoxylates are water soluble provided the alkyl chain length of the compound is not long (usually a C_{12} chain is adequate for reasonable solubility at sufficient EO content).

Ethylene Oxide–Propylene Oxide Copolymers (EO/PO). As mentioned above these may be regarded as polymeric surfactants. These surfactants are sold under various trade names, namely Pluronics (Wyandotte), Synperonic PE (ICI), Ploxomers, etc. Two types may be distinguished: those prepared by reaction of polyoxypropylene glycol (dinfunctional) with EO or mixed EO/PO, giving block copolymers with the structure,



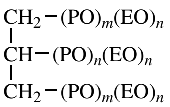
$$HO(CH_2CH_2O)_n\text{—}(CH_2\underset{CH_3}{\underset{|}{C}}HO)_m\text{—}(CH_2CH_2)_nOH$$

abbreviated $(EO)_n(PO)_m(EO)_n$

Various molecules are available, where n and m are varied systematically.

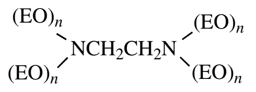
The second type of EO/PO copolymers are prepared by reaction of polyethylene glycol (difunctional) wit PO or mixed EO/PO. These will have the structure $(PO)_n(EO)_m(PO)_n$ and they are referred to as reverse Pluronics.

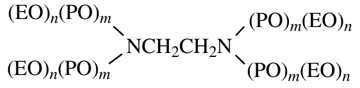
Trifunctional products are also available where the starting material is glycerol. These have the structure:



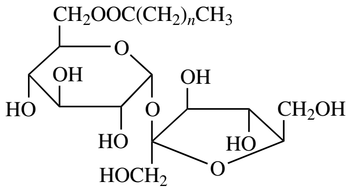
$$\begin{array}{l} CH_2-(PO)_m(EO)_n \\ | \\ CH-(PO)_n(EO)_n \\ | \\ CH_2-(PO)_m(EO)_n \end{array}$$

Tetrafunctional products are available where the starting material is ethylene diamine. These have the structures:

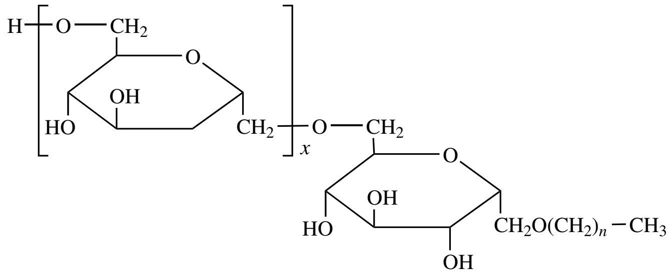




Surfactants Derived from Mono- and Poly-saccharides. Several surfactants were synthesized starting from mono- or oligo-saccharides by reaction with the multifunctional hydroxyl groups. The technical problem is one of joining a hydrophobic group to the multihydroxyl structure. Several surfactants were made, eg, estrification of sucrose with fatty acids or fatty glycerides to produce sucrose esters having the following structure,



The most interesting sugar surfactants are the alkyl polyglucosides (APG) having the following structure:



These are produced by reaction of a fatty alcohol directly with glucose. The basic raw material are glucose and fatty alcohols (which may be derived from vegetable oils) and hence these surfactants are sometimes referred to as "environmentally friendly". A product with $n = 2$ has two glucose residues with four OH groups on each molecule (ie, total 8 OH groups). The chemistry is more complex and commercial products are mixtures with $n = 1.1$ to 3. The properties of APG surfactants depend upon the alkyl chain length and the average degree of polymerization. APG surfactants have good solubility in water and they have high cloud points (> 100°C). They are stable in neutral and alkaline solutions but are unstable in strong acid solutions. APG surfactants can tolerate high electrolyte concentrations and they are compatible with most types of surfactants.

5.5. Speciality Surfactants. Flurocarbon and silicone surfactants can lower the surface tension of water to values below 20 mNm^{-1} most surfactants described above lower the surface tension of water to values above 20 mNm^{-1}, typically in the region of 25–27 mNm^{-1}. The fluorocarbon and silicone surfactants are sometimes referred to as superwetters as they cause enhanced wetting and spreading of their aqueous solution. However, they are much more expensive than conventional surfactants and they are only applied for specific applications whereby the low surface tension is a desirable property.

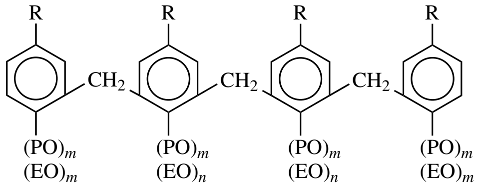
Fluorocarbon surfactants have been prepared with various structures consisting of perfluoroalkyl chains and anionic, cationic, amphoteric and polyethylene oxide polar groups. These surfactants have good thermal and chemical stability and they are excellent wetting agents for low energy surfaces.

Silicone surfactants, sometimes referred to as organosilicones are those with polydimethylsilixane backbone. The silicone surfactants are prepared by incorporation of a water soluble or hydrophilic group into a siloxane backbone. The latter can also be modified by incorporation of a paraffinic hydrophobic chain at the end or along the polysiloxane back bone. The most common hydrophilic groups are EO/PO and the structures produced are rather complex and most manufacturers of silicone surfactants do not reveal the exact structure. The mechanism by which these molecules lower the surface tension of water to low values is far from being well understood. The surfactants are widely applied as spreading agents on many hydrophobic surfaces.

Incorporating organophilic groups into the backbone of the polydimethyl siloxane backbone can give products that exhibit surface active properties in organic solvents.

5.6. Polymeric Surfactants. In recent years there has been considerable interest in polymeric surfactants due to their wide application as stabilizers for suspensions and emulsions. Various polymeric surfactants have been introduced and they are marketed under special trade names (such as Hypermers of ICI). One may consider the block EO/PO molecules (Pluronics) as polymeric surfactants, but these generally do not have high molecular weights and they seldom produce speciality properties. Silicone surfactants may also be considered as polymerics. However, the recent development of speciality polymeric surfactants of the graft type (“comb” structures) have enabled one to obtain specific applications in dispersions. An example of such molecules is the graft copolymer of poly (methyl methacrylate) backbone with several PEO side chains (sold under the trade name Hypermer CG6 by ICI) which has excellent dispersing and stabilizing properties for concentrated dispersions of hydrophobic particles in water. Using such dispersant, one can obtain highly stable concentrated suspensions. These surfactants have been modified in several ways to produce molecules that are suitable as emulsifiers, dispersants in extreme conditions such as high or low pH values, high electrolyte concentrations, temperatures etc. Other polymeric surfactants that are suitable for dispersing dyes and pigments in nonaqueous media have also been prepared, whereby the side chains were made oil soluble such as polyhydroxystearic acid.

Another important class of polymeric surfactants that are used for demulsification are those based on alkoxylated alkyl phenol formaldehyde condensates, with the general structure:



Several other complex polymerics are manufactured for application in the oil industry, eg, polyalkylene glycol modified polyester with fatty acid hydrophobes, polyesters, made by polymerization of polyhydroxy stearic acid, etc.

6. Health and Safety Factors

6.1. Dermatological Aspects. A large fraction of dermatological problems in normal working life can be related to exposure of unprotected skin to surfactant solutions (2). Several formulations contain significant amount of surfactants, eg, cutting fluids, rolling oil emulsions, some household cleaning formulations, and some personal care products. Skin irritation of various degrees of seriousness are common, and in some cases allergic reactions may also appear. The physiological aspects of surfactants on the skin are investigated by various dermatological laboratories, starting with the surface of the skin and progressing via the horny layer and its barrier function to the deeper layer of the basal cells. Surfactant classes that are generally known to be mild to the skin include polyol surfactants (alkyl polyglucosides), zwitterionic surfactants (betaines, amidobetaines and isethionates), and many polymeric surfactants. Alcohol ethoxylates are relatively mild, but not as mild as the polyol based nonionics (the alkyl polyglucosides). In addition, alcohol ethoxylates may undergo oxidation giving byproducts (hyperoxides and aldehydes) which are skin irritants. These classes are commonly used in personal care and cosmetic formulations.

For a homologous series of surfactants there is usually a maximum in skin irritation at a specific alkyl chain length; maximum irritation usually occurs at C_{12} chain length. This reflects the maximum in surface activity at this chain length and the reduction in the cmc. Anionic surfactants are generally more skin irritants than nonionics. For example sodium dodecyl sulfate which is commonly used in toothpaste has a relatively high skin toxicity. In contrast, the ether sulfates are milder and they are recommended for use in hand dishwashing formulations. Sometimes addition of a mild surfactant (such as alkyl polyglucoside) can cause large improvement in the dermatological properties. Some amphoteric surfactants such as betaines can also reduce the skin irritation of anionic surfactants.

6.2. Aquatic Toxicity. Aquatic toxicity is usually measured on fish, daphnia and algae. The toxicity index is expressed as LC_{50} (for fish) or EC_{50} (for daphnia and algea), where LC and EC stand for lethal and effective concentration, respectively. Values below 1 mg L^{-1} after 96 h testing on fish and algae and 48 h on daphnia are considered toxic. Environmentally benign surfactants should preferable be above 10 mg L^{-1}.

6.3. Biodegradability. Biodegradation is a process carried out by bacteria in nature. By enzymatic reactions, a surfactant molecule is ultimately converted to carbon dioxide, water, and oxides of the other elements. If the surfactant does not undergo natural biodegradation than it is stable and persists in the environment. For surfactants the rate of biodegradation varies from 1–2 h for fatty acids, 1–2 days for linear alkyl benzene sulfonates and for several month for branched alkyl benzene sulfonate. The rate of biodegradation depends on the surfactant concentration, pH, and temperature. The temperature effect is particularly important, since the rate can vary by as much a factor of five between summer and winter in Northern Europe.

Two criteria are important when testing for biodegradation: (*1*) Primary degradation that results in loss of surface activity; (*2*) ultimate biodegration, ie, conversion to carbon dioxide which can be measured using closed bottle tests.

The rate of biodegradation depends on the surfactant structure. For example, the surfactant must be water soluble. Lipophilic amphiphiles such as fluorocarbon surfactants may accumulate in lipid compartments of the organism and break down very slowly. The initial degradation may also lead to intermediates with much lower water solubility and these degrade very slowly. An example is the alkyl phenol ethoxylates, which degrade by oxidative cleavage from the hydroxyl end of the polyoxyethylene chain. This leads to a compound with much smaller EO groups that is very lipophilic and degrades at a very slow rate.

A third important factor in biodegradation is the presence of cleavable bonds in the alkyl chain which depend on branching. Extensive branching of the alkyl chain tends to reduce the rate of biodegradation. This is probably due to steric hinderance preventing close approach of the surfactant molecule into the active site of the enzyme.

7. Applications

7.1. Emulsions. Emulsions are dispersions of two immiscible liquids. The disperse droplets cover a wide rage of droplet sizes usually in the region 0.1–5 μm, with an average of 2–3 μm. To disperse a liquid into another liquid one requires the application of a surfactant that is referred to as the emulsifier. Energy must also be applied to the system using a high speed stirrer or homogenizer. This is due to the nonspontaneous nature of the emulsification process which can be understood from a consideration of the free energy of formation of the emulsion, ΔG^{form}. The latter is made from two contributions, an energy term that is given by $\Delta A\gamma$ (where ΔA is the increase in interfacial area on dispersion of the bulk oil into small droplets and γ is the interfacial tension) and an entropy term $T\Delta S$ (where T is the absolute temperature),

$$\Delta G^{form} = \Delta A\gamma - T\Delta S \qquad (51)$$

Since γ is positive, then $\Delta A\gamma$ is large and positive and this exceeds $-T\Delta S$, ie, ΔG^{form} is also large and positive and the formation of an emulsion requires energy to disperse the droplets. The amulsifier lowers γ and this reduces $\Delta A\gamma$ and this reduces the energy reqired for emulsification. The emulsifier also prevents coalescence of the droplets during dispersion.

Several methods may be applied for selection of an emulsifier for a particular oil and the most useful procedure is to apply the hydrophilic–lipophilic-balance (HLB) concept. The HLB gives a measure of the relative proportion of hydrophilic to lipophilic groups. For a simple emulsifier such as an alcohol ethoxylate $C_{12}H_{25}{-}O{-}(CH_2{-}CH_2)_4{-}H$, the hydrophilic groups have a weight % of $\sim$50 and the HLB number is simply the weight percent divided by 5, ie, $\sim$10. For oil-in-water (O/W) emulsions the HLB range is 8–18, whereas the for water-in-oil (W/O) emulsions this range is 3–6. The optimum HLB number for producing the most stable emulsion depends on the nature of the oil.

The optimum HLB number is obtained by using two surfactant molecules, one with a low HLB number (referred to as HLB_1) and one with a high HLB number (referred to as HLB_2). The average HLB number is calculated from the weight fractions x_1 and x_2 of the two surfactants,

$$HLB_{av} = x_1 HLB_1 + x_2 HLB_2 \tag{52}$$

Emulsions are then prepared using the various surfactant mixtures and their stability determined using droplet size analysis versus time measurements or simply by observing emulsion separation. With O/W emulsions, the stability of the emulsion increases as the proportion of the surfactant with the high HLB number increases and it reaches a maximum at an optimum ratio of the two surfactants (optimum HLB number) after which the stability decreases with further increase of the surfactant with the high HLB number.

Surfactants are also essential for prevention of flocculation of emulsions. In the absence of an emulsifier, the droplets undergo rapid flocculation (diffusion controlled process), and this results to strong flocculation. The latter is due to the van der Waals attraction which increases rapidly with decrease of separation distance between the droplets. To overcome this attraction, one needs a strong repulsive force that operates at intermediate distances of separation thus overcoming the close separation between the droplets. Two repulsive forces can be distinguished, namely electrostatic and steric interaction. The electrosatic repulsion arises when electrical double layers are produced around the droplets as a result of charge separation. This can occur when the emulsifier is ionic in nature. At low electrolyte concentrations ($<10^{-2}$ mol dm^{-3} 1:1 electrolyte, eg, NaCl) the repulsive force is significant and an energy barrier is produced between the droplets, thus, preventing their flocculation. An alternative and more effective way for stabilizing the emulsion is to use nonionic surfactants or polymers which produce adsorbed layers with thickness δ. When two droplets approach each other to a distance of separation h that is smaller than 2δ, strong repulsion occurs as a result of two main effects: (*1*) Unfavorable mixing of the chains when these are in good solvent conditions. (*2*) Reduction in configuration enetropy on overlap of the chains.

Surfactants are also essential in reducing or eliminating coalescence of the emulsion droplets. Coalescence is the result of thinning and disruption of the liquid film between the droplets with the ultimate joining of two or more droplets and finally oil separation occurs. This process is prevented by the surfactant film which produces high elasticity at the O/W interface and prevents any surface or film fluctuation. In many cases, lamellar liquid crystalline phases that are produced by using surfactant mixtures can prevent coalescence by creating a strong barrier as a result of the multilayer structure of the liquid crystalline phase.

7.2. Suspensions. Surfactants are essential for the preparation of solid/liquid dispersions (suspensions). The latter are generally prepared using two main procedures: (*1*) Building up of particles from molecular units. (*2*) Dispersion of bulk performed powder in a liquid followed by dispersion and wet milling (comminution) to produce smaller particles. An example of the first system is the production of polymer latex dispersions by emulsion or dispersion polymerization. The monomer is emulsified in an aqueous solution containing a surfactant to produce an emulsion of the monomer. An initiator is added to initiate the polymerization process. In some cases, initiation occurs in the micelles which are swollen by the monomer. The number of particles produced and hence their size is determined by the number of the micelles in solution. In dispersion polymerization, the monomer is mixed with a solvent in which the resulting polymer is insoluble. A surfactant (protective colloid) and initiator is added. The surfactant prevents flocculation of the polymer particles once formed. Again the size of the particles produced depends on the nature and concentration of the surfactant used.

The dispersion of bulk solids in a liquid requires the presence of a surfactant that aids the wetting of the powder into the liquid. Both external and internal surfaces of the aggregates and agglomerates must be completely wetted by the dispersion medium and this requires molecules that lower the dynamic surface tension of the liquid and the solid/liquid interfacial tension (by rapid adsorption on the particles). Any aggregates or agglomerates are broken down by using high speed mixers. The dispersed particles are then subdivided into smaller units (to reach a particle size in the region of 1–2 μm, depending on application) by a wet milling process. The surfactant aids the process of comminution by fast adsorption into cracks of the crystals which facilitates crack propagation.

The surfactant also prevents aggregation of the particles, once formed by producing a strong repulsive force. As with emulsions, two stabilization mechanisms can be considered, namely electrostatic (when using ionic surfactants) and steric when using nonionic surfactants and polymers.

Surfactants can also prevent Ostwald ripening (crystal growth) of the particles by strong adsorption on the active sites of the crystals. Ostwald ripening results from the difference in solubility between the small and the larger particles. The smaller particles have higher solubility than the larger ones (due to the higher radius of curvature of the smaller particles) and on storage, the smaller particles tend to dissolve and become deposited on the larger ones. This results in a shift in the particle size distribution to larger values and this could affect the physical stability of the suspension (by enhancing sedimentation) as well as its bioefficacy (with drugs and agrochemicals).

7.3. Microemulsions. Microemulsions are transparent or translucent systems covering the size range 5–50 nm. Unlike macroemulsions which are only kinetically stable, microemulsions are thermodynamically stable and they form spontaneously. The driving force of their formation is the low or ultralow interfacial tension, usually in the range 10^{-4}–10^{-2} mNm^{-1}. This results in a low interfacial energy ($\Delta A\gamma$) which is overcompensated by the negative entropy of dispersion ($-\ T\Delta S$). Thus the free energy term of formation of microemulsions ΔG^{form} becomes zero or negative and this results in their spontaneous formation (no energy is required to produce the system) and their thermodynamic stability.

To achieve the above low interfacial energy, it is convenient to use two surfactant molecules, one predominantly water soluble such as sodium dodecyly sulfate, SDS and one oil soluble (to be referred to as the cosurfactant) such as pentanol. This reduction in interfacial tension on addition of the cosurfactant can be explained if one considers the $\gamma - \log C$ curves (where C is the surfactant concentration). For SDS alone the interfacial tension decreases with increase in C and once the cmc is reached, γ remains constant. This limiting value of γ is seldom below 0.1 mNm^{-1} for most O/W systems. However, on addition of pentanol the $\gamma - \log C$ is shifted to lower values and the cmc is reduced. By gradual addition of pentanol γ can reach very low values and it may even become negative under transient conditions. In this case the microemulsion is formed spontaneously and the system is thermodynamically stable.

The selection of surfactants for producing O/W or W/O microemulsions is not simple and one needs to establish the phase diagram of the ternary system oil–water–surfactant–cosurfactant to arrive at the regions of formation of O/W or W/O microemulsions. A useful concept for selection of surfactants is based on the critical packing parameter (CPP) of the molecules,

$$CPP = \frac{v}{l_c a} \tag{53}$$

Where v is the volume of the hydrocarbon chain, l_c is its extended length (v/l_c is the cross sectional area of the hydrocarbon chain) and a is the cross sectional area of the head group. For O/W systems, $\text{CPP} \leq (1/3)$, whereas for W/O systems $\text{CPP} > 1$. Thus by adjusting the composition of surfactant and cosurfactant one can arrive at the right CPP.

7.4. Personal Care and Cosmetics. Cosmetic and toiletry products are generally designed to deliver a function benefit and to enhance the psychological well-being of consumers by increasing their aesthetic appeal. Since cosmetic products come in thorough contact with various organs and tissues of the human body, a most important consideration for choosing ingredients to be used in these formulations is their medical safety. These ingredients must not cause any allergy, sensitization, or irritation and they must be free of any impurities that cause toxic effects. This is particularly the case for surfactants that can be used in cosmetic products.

One of the main areas of interest of cosmetic formulations is their interaction with the skin. The top layer of the skin, which is the main barrier to water loss, is the stratum corneum, which protects the body from chemical and biological attack. This layer is very thin, approximately 30 μm, and it consists of ~10% by weight of lipids that are organized in a bilayer structure (lamellar liquid crystalline) which at high water content is soft and transparent. When a cosmetic formulation is applied to the skin, it interacts with the stratum corneum and it is essential to maintain the “liquid-like” nature of the bilayer and prevent any crystallization of the lipids. This happens when the water content is reduced below a certain level. Any surfactant that causes disruption of the stratum corneum must be avoided and this is usually accompanied by skin irritation and the skin will feel “dry”.

Several cosmetic formulations can be idenified of which the following is worth mentioning: (*1*) Lotions are usually O/W emulsions that are formulated in such a way to give a shear thinning system, ie, the viscosity decreases with application of shear rates (on application). (*2*) Hand creams are formulated as O/W or W/O emulsions with special surfactant systems and thickeners to give a shear thinning system, but with viscosities that are order of magnitude higher than that of lotions. (*3*) Shampoos are normally a “gelled” surfactant solution of well-defined association structures, eg, rod-shaped micelles. A thickener such as a polysaccharide may be added to increase the relaxation time of the system. (*4*) Foundations are complex systems consisting of a suspension–emulsion system (sometimes referred to as suspo-emulsion). Pigment particles are usually dispersed in the continuous phase of an O/W or W/O emulsion. Volatile oils such as cyclomethicone are usually used. The system should be thixotropic (decrease of viscosity with applied shear and its recovery on stopping the shear) to ensure uniformity and good leveling.

Several classes of surfactants are used to formulate the above system and as mentioned before they should give no allergy, sensitization, or skin irritation. Conventional surfactants of the ionic, amphoteric and nonionic types can be used provided they satisfy the above criteria of safety. Nonionic surfactants are usually preferred, since they are uncharged and they have low skin sensitization potential. Phosphoric acid esters are also used in some cosmetic formulations, since these are similar to the phospholipids that constitute the natural builiding blocks of the stratum corneum. Glycerine esters, in particular the triglyceride, are also used in many cosmetic formulations. These surfactants are important ingredients of the sebum, the natural lubricant of the skin. Macromolecular surfactants possess considerable advantages for use in cosmetic ingredients. The most commonly used materials are the ABA block copolymers, such as the Pluronics or Synperonic PE (PEO–PPO–PEO block copolymers). These polymeric surfactants have much lower toxicity, sensitization and irritation potentials. Polymeric surfactants based on polysaccharides, such as hydrophobically modified inulin (polyfructose) (INUTEC SP1, ORAFTI, Belgium) have been recently applied in many cosmetic formulations.

Recent years have seen a great trend towards using silicone oils for many cosmetic emulsions. These silicone oils are best emulsified using silicone surfactants such as siloxane–poly(ethylene oxide) copolymer.

Another important class of surfactants in cosmetics are the phospholipids (eg, lecithin obtained from egg yolk or soybean) which are used as emulsifiers as well as for the formation of liposomes and vesicles. Liposomes are multilammellar bilayers of phospholipids which on sonication produce singular bilayers or vesicles. They are ideal systems for cosmetic applications. They offer a convenient method for solubilizing water insoluble active substances in the hydrocarbon core of the bilayer. They will always form a lamellar liquid crystalline structure on the skin and, therefore, they do not disrupt the structure of the stratum corneum. Phospholipid liposomes may be used as an indicator for studying skin irritation by surfactants.

7.5. Pharmaceuticals.

Several classes of surfactants can be identified in pharmaceutical application, namely drugs which are themselves surface active, surfactants that are used for formulation of suspensions, emulsions, semisolids and gels and naturally occurring surfactants in the body. Many drugs are surface active, eg, chlorpromazine, diphenylmethane derivatives and tricyclic antidepressants. These molecules exhibit surface active properties that are similar to surfactants, eg, they accumulate at interfaces and produce aggregates (micelles) at critical concentration. Evidence for this was obtained from surface tension and light scattering measurements, which showed reduction in surface tension and increase in light scattering at a critical concentration. However, the aggregation number of the drug micelles is lower than that obtained with surfactants, usually in the region of 9–12 monomer units.

Both surface activity and micellization have implications on the biological efficacy of many drugs. Surface active drugs tend to bind hydrophobically to proteins and other biological macromoleules. They tend to associate with other amphipathic molecules such as other drugs, bile salts, or with receptors.

Surfactants are used for the formulation of many pharmaceutical formulations such as suspensions, emulsions, multiple emulsions, semisolid and gels for topical application. In all cases the surfactant must be approved by the Food and Drug Adminstration (FDA) and this limits the choice in pharmaceutical applications. Several surfactant molecules have been approved by the FDA, both of the ionic and nonionic type. The latter are perhaps the most widely used molecules in pharmaceuticals, eg, sorbitan esters (Spans) and their ethoxylated analogues (Tweens). Polymeric surfactants of the PEO–PPO–PEO block type or Poloxamers (ICI, U.K.) are also used in many formulations. Many pharmaceutical emulsions, eg, lipid and anaesthetic emulsions, are formulated using egg lecithin which has to be pure and free from any toxic impurities.

Lecithin is also used for the preparation of liposomes and vesicles which are ideal for drug delivery. This is due to their high degree of biocompatability, in particular for intravenous application. Liposomes can solubilize lipid soluble drugs in the hydrocarbon core of the bilayers, whereas water soluble drugs can be solubilized in the aqueous film between the bilayers.

One of the most useful application of surfactants in pharmaceuticals is solubilization of poorly water soluble drugs by surfactant micelles. Solubilization is the preparation of a thermodynamically stable isotropic solution of a substance (normally insoluble or sparingly soluble in a given solvent) by incorporation of an additional amphiphilic component(s). It is the incorporation of the compound, referred to as solubilizate or substrate, within a micellar or reverse micellar system. The compound can be incorporated into various locations within the micelle depending on its structure and polarity. For nonpolar solubilizates, the preferred location is the hydrocarbon core of the micelle. For a polar substrate, the preferred location is in the PEO core of the micelle or simply adsorbed at its surface. For a semipolar compound, the molecule can be incorporated between the surfactant molecules in the micelle, either in short or deep penetration.

Several factors affect the extent of solubilization such as the structure of the molecule, the structure of the surfactant, temperature and addition of electrolytes and nonelectrolytes. With nonpolar compunds, solubilzation increases with increase of the alkyl chain length of the surfactant. For the same alkyl chain length solubilization increases in the order: anionic $<$ cationic $<$ nonionic. Increase in temperature increases the solubility of the compound and this results in increase of solubilization. Most electrolytes lower the cmc of the surfactant and they may increase the aggregation number (and size) of the micelle. This results in an increase of solubilization.

The presence of micelles and surfactant monomers in a drug formulation can have pronounced effects on the biological efficacy. Surfactants (both micelles and monomers) can influence the dissolution and disintegration of solid dosage forms by controlling the rate of precipitation. They can also increase membrane permeability and affect membrane integrity. The release of poorly soluble drugs from tablets and capsules (oral use) can be increased in the presence of surfactants. The reduction in aggregation on disintegration of tablets increases the surface area and this enhances the rate of solution. Lowering of the surface tension aids penetration of water into the drug mass. Above the cmc, an increase in flux by solubilization can lead to an increase in the dissolution rate. Several naturally occurring surfactants (in the body) can be identified, such as bile salts, phospholipids and cholesterol, which play an important role in various biological processes. The interactions with other solutes, such as drug molecules and with membranes are also very important. Bile salts play important roles in physiological functions and drug absorption. It is generally agreed that bile salts aid fat absorption. Mixed micelles of bile salts, fatty acids and monoglycerides act as vehicles for fat absorption. Another important naturally occurring class of surfactants that are widely found in biological membranes are the lipids, which include phosphatidylcholine (lecithin), lysolecithin, phosphatidylethanolamine and phosphatidyl inositol. These lipids are used as emulsifiers for intravenous fat emulsions, anaethic emulsions as well as production of liposomes and vesicles for drug delivery. Phospholipids also play an important role in lung fuctions. The surface active material to be found in the aveolar lining of the lung is a mixture of phospholipids, natural lipids and proteins. Lowering of surface tension by the lung surfactant system and the surface elasticity of surface layers assist aveolar expansion and contraction. Deficiency of lung surfactants in newborns leads to respiratory distress syndrome. It has been suggested that instillation of phospholipid surfactants could cure the problem.

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Table 1. **Cmc Values of Some Surface Active Agents**

Surface active agent	cmc/mol dm^{-3}
Anionic	
sodium octyl-l-sulfate	1.30×10^{-1}
sodium decyl-l-sulfate	3.32×10^{-2}
sodium dodecyl-l-sulfate	8.39×10^{-3}
sodium tetradecyl-l-sulfate	2.05×10^{-3}
Cationic	
octyl trimethyl ammonium bromide	1.30×10^{-1}
decetryl trimethyl ammonium bromide	6.46×10^{-2}
dodecyl trimethyl ammonium bromide	1.56×10^{-2}
hexactecyltrimethyl ammonium bromide	9.20×10^{-4}
Nonionic	
octyl hexaoxyethylene glycol monoether, C_8E_6	9.80×10^{-3}
decyl hexaoxyethylene glycol monoether, $C_{10}E_6$	9.00×10^{-4}
decyl nonaoxyethylene glycol monoether, $C_{10}E_9$	1.30×10^{-3}
dodecyl hexaoxyethylene glycol monoether, $C_{12}E_6$	8.70×10^{-5}
octylphenyl hexaoxyethylene glycol monoether, C_8E_6	2.05×10^{-4}

Table 2. **Thermodynamic Quantities for Micellization of Octylhexaoxyethylene Glycol Monoether**

Temp/$^\circ$C	ΔG°/KJ mol^{-1}	ΔH°/KJ mol^{-1} (from cmc)	ΔH°/KJ mol^{-1} (from calorimetry)	$T\Delta S^\circ$/KJ mol^{-1}
25	$-21.3 + 2.1$	$8.0 + 4.2$	$20.1 + 0.8$	$41.8 + 1.0$
40	$-23.4 + 2.1$		$14.6 + 0.8$	$38.0 + 1.0$

Table 3. **Change of Thermodynamic Parameters of Micellization of Alkyl Sulfoxide with Increasing Chain Length of the Alkyl Group**

Surfactant	ΔG/KJ mol^{-1}	ΔH°/KJ mol^{-1}	$T\Delta S^\circ$/KJ mol^{-1}
$C_7H_{15}S(CH_3)O$	−15.9	9.2	25.1
$C_8H_{17}S(CH_3)O$	−18.8	7.8	26.4
$C_9H_{19}S(CH_3)O$	−22.0	7.1	29.1
$C_{10}H_{21}S(CH_3)O$	−25.5	5.4	30.9
$C_{11}H_{23}S(CH_3)O$	−28.7	3.0	31.7

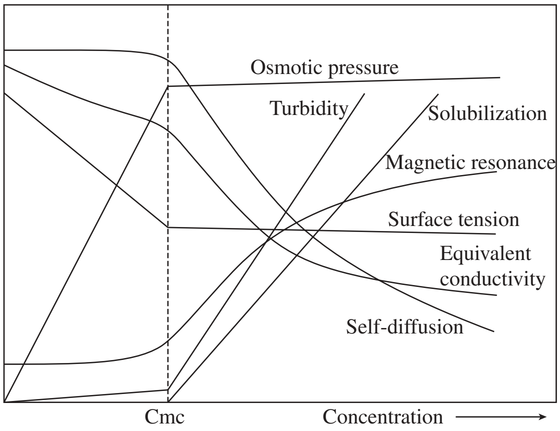

Fig. 1. Changes in the concentration dependence of a wide range of physico-chemical changes around the critical micelle concentration (cmc), after Lindman and co-workers (1).

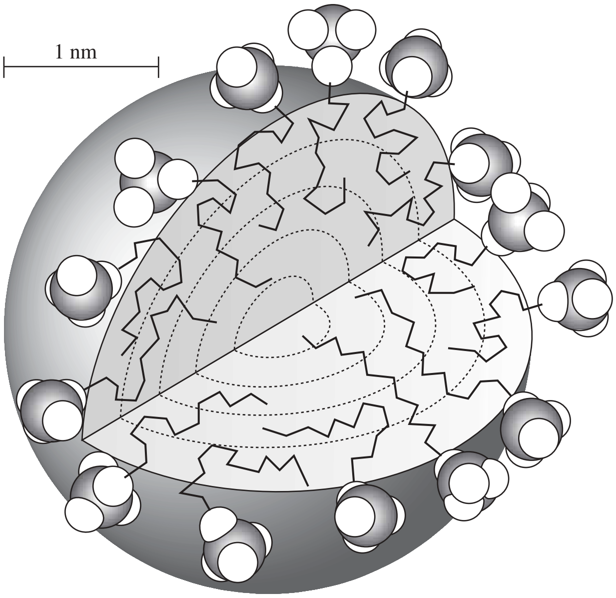

Fig. 2. Illustration of a spherical micelle for dodecyl sulfate (1).

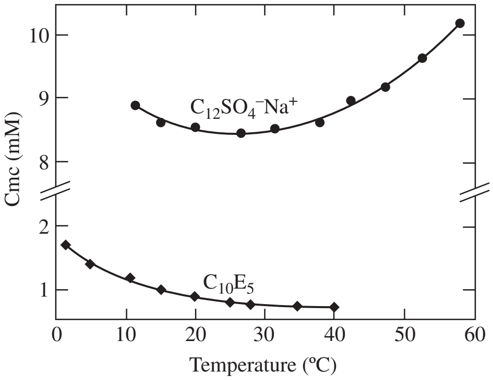

Fig. 3. Temperature dependence of the cmc of SDS and $C_{10}E_5$ (1).

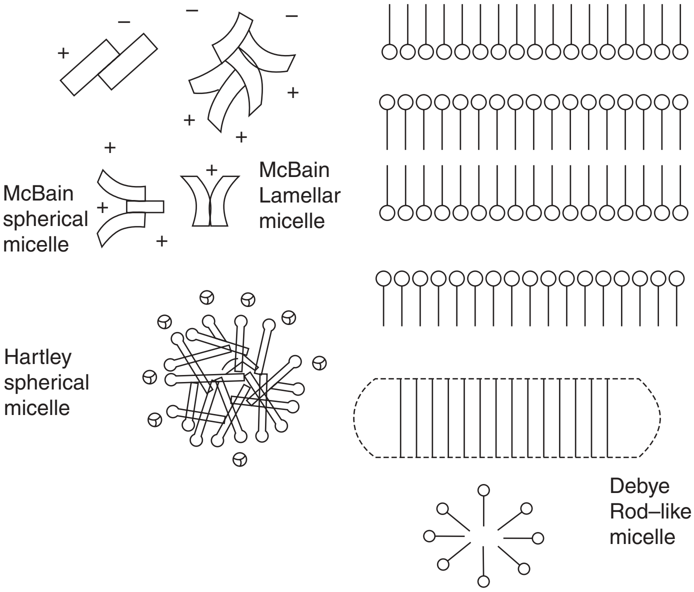

Fig. 4. Various shapes of micelles, following McBain (2), Hartley (2), and Debye (2).

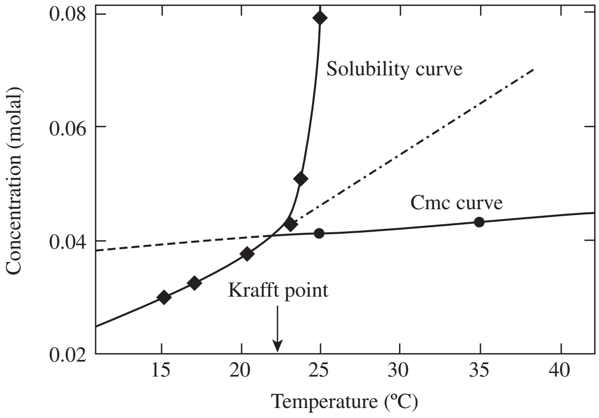

Fig. 5. Solubility and cmc versus temperature for sodium decyl benzene sulfonate in water.

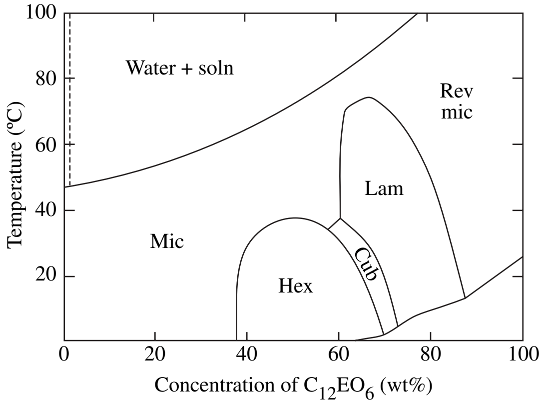

Fig. 6. Phase diagram for $C_{12}EO_6$–water system.

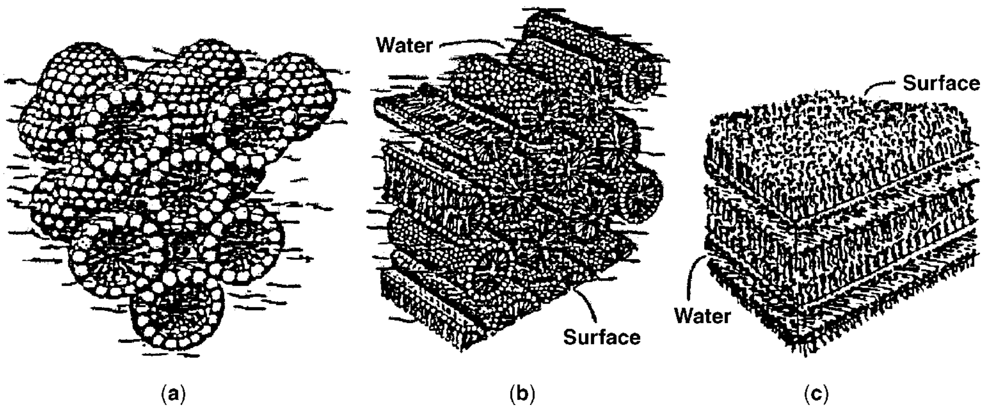

Fig. 7. Schematic representation of the structure of liquid crystalline phases.

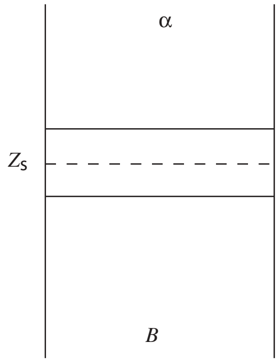

Fig. 8. Gibbs convention for an interface.

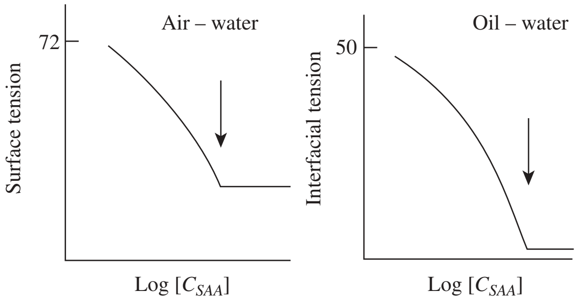

Fig. 9. Variation of surface and interfacial tension with log [C_{SAA}] at the air–water and oil–water interface.

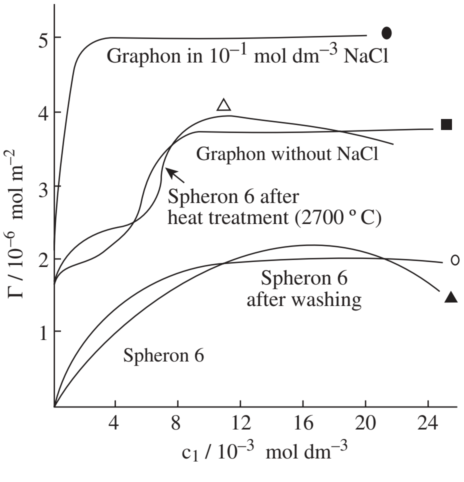

Fig. 10. Adsorption isotherms for sodium dodecyl sulfate (SDS) on carbon substrates. Graphon in 10^{-1} mol dm^{-3} NaCl (●); and without added electrolyte (△). Spheron 6 (▲) and after washing (○) and after heat treatment at 2700°C.

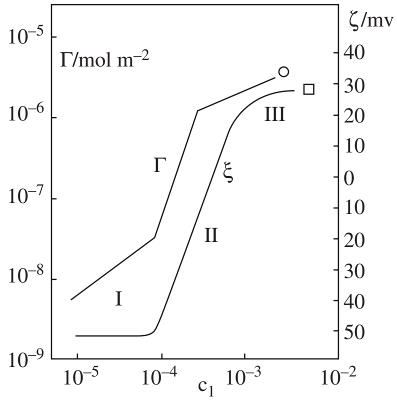

Fig. 11. The adsorption isotherm for sodium dodecyl sulfonate (SDSe) on alumina (○) and the corresponding ζ-potential of alumina particles (□) as a function of the equilibrium surfactant concentration; pH = 7.2 and 2×10^{-3} mol dm^{-3} ionic strength.

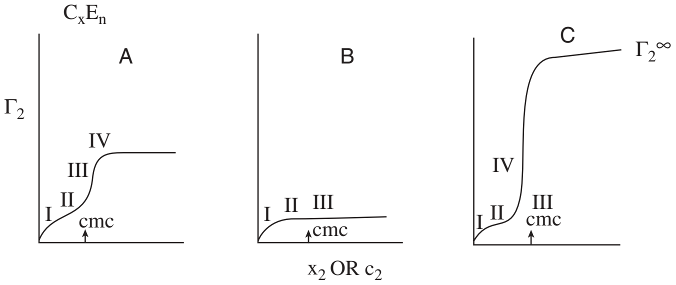

Fig. 12. Adsorption isotherms, corresponding to the three adsorption sequences shown in Fig. 13 (I–IV), indicating the different orientation; the cmc is indicated by an arrow.

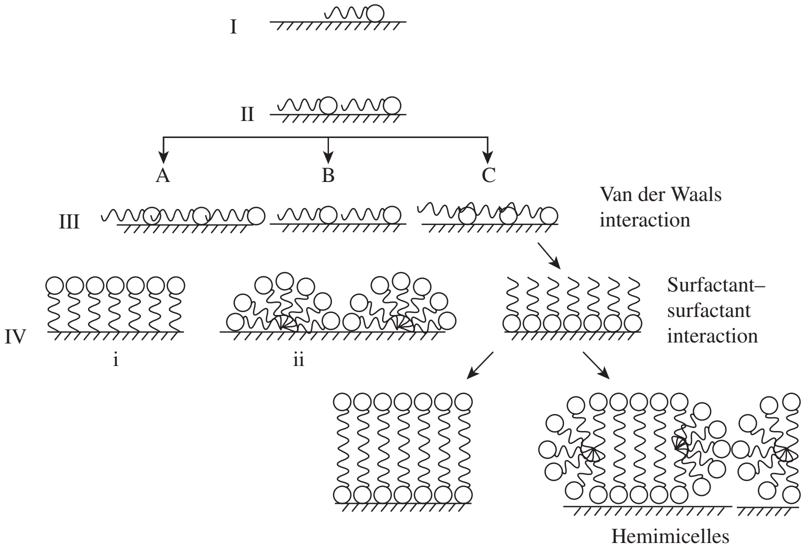

Fig. 13. Model for the adsorption of nonionic surfactants showing orientation of surfactant molecules at the surface. I–V are the successive stages of adsorption, and sequence A–C corresponds to situations where there are relatively weak, intermediate, and strong interactions between the adsorbent and the hydrophilic moiety of the surfactant.