Chapter 1

Introduction

1.1 Definition of a surfactant

The word surfactant does not appear in most dictionaries. This is because it is not only a technical term, but a diminutive form of the the phrase surface active agent [Clint, 1992]. Surfactants are among the most versatile of the products of the chemical industry, appearing in diverse products such as motor oils, pharmaceuticals, detergents and ore flotation to name a few [Rosen, 2004].

A surfactant is a substance that, when present at low concentrations in a system has the property of adsorbing onto the surfaces or interfaces of the system and altering to a marked degree the interfacial free energy of the interfaces. The interfacial free energy is the minimum amount of work required to create an interface. The interfacial free energy per unit area is the interfacial tension between the two phases (the word surface tension is used when one of the phase is air or gas). In addition to the surface adsorption properties, surfactants have the remarkable ability to self assemble in aqueous solution. The structures spontaneously formed by surfactants in solution are called as micelles [Tsuji, 1998].

1.2 Structure and behaviour of surfactants

Surfactants have a characteristic molecular structure consisting of a structural group with little affinity for water known as the hydrophobic group (usually called the tail group), together with a group that has strong attraction for water known as the hydrophilic group (usually called the head group). This is known as amphipathic structure. On dissolution in water, the hydrophobic group in the interior of water causes distortion of the water liquid structure (i.e hydrogen bonding is disrupted), increasing the free energy of the system. It means that less work is needed to bring a surfactant molecule than a water molecule to the surface. The
surfactant therefore begins to concentrate on the surface. As less work is needed to bring the molecules to the interface, less work is needed to create unit area of surface (surface tension is reduced). At the same time, presence of hydrophilic group prevents the surfactant from being expelled completely from the water as a separate phase, since it requires dehydration of the hydrophilic group. The amphipathic structure of the surfactant results in concentration of the surfactant at the surface (resulting in surface tension reduction) and orientation of the molecule at the interface with the hydrophilic group in water and hydrophobic group oriented away from water.

1.2.1 Hydrophilic group

The hydrophilic group of the surfactant is referred to as the head group and is highly polar or charged. Depending on the nature of the head group, surfactants can be classified as

1. Anionic surfactants: The head group has a negative charge. The counterion has a positive charge. e.g. sodium and potassium salts of fatty acids. The counterion is $Na^+$ or $K^+$ and the head group is the carboxylate group ($R - COO^-$). Usually used in cleaning formulations.

2. Cationic surfactants: The head group has a positive charge. The counterion has a negative charge. e.g. quaternary ammonium salts like cetyl trimethylammonium bromide. The counterion is $Br^-$ and the head group is quaternary ammonium ion ($R_4 - N^+$). The positive charge gives the surfactant a strong substantivity on negatively charged fibres, such as hair and cotton. Used as fabric and hair conditioner.

3. Zwitterionic surfactants: The head group has both positive and negative charges. e.g. betaines ($R - N^+ (CH_3)_2 - CH_2 COO^-$) and sulfobetaines ($R - N^+ (CH_3)_2 - CH_2 SO_3^-$). Milder on skin than anionics, have low eye-sting effects, which leads to its use in toiletries and baby shampoos.

4. Nonionic surfactants: The head group has no apparent ionic charge. e.g. Alkyl alcohol ethoxylates like polyoxyethylene cetyl ether ($R - (OCH_2 CH_2)_n OH$). The ethoxylate group is the head group. Used in low temperature detergency and as an emulsifiers.

1.2.2 Hydrophobic group

The hydrophobic group is also referred as the tail group. Differences in nature of tail groups are usually less pronounced than in the nature of the head group. Some of the different structures are

1. Straight chain, long alkyl groups ($C_8 - C_{20}$).
2. Branched chain, long alkyl groups \((C_8 - C_{20})\).
3. Long chain \((C_8 - C_{15})\), alkyl benzene residues.
4. High Molecular weight propylene oxide polymers.
5. Long-chain perfluoroalkyl groups.

### 1.2.3 Electrical double layer

At an interface there is always an unequal distribution of electrical charges between the two phases. This unequal distribution causes one side of the interface to acquire a net charge of a particular sign and the other side a net charge of the opposite sign, giving rise to potential across the interface and an electrical double layer. Interface charge originates via two processes:

1. Ionisation or dissociation of a functional group at the interface
2. Ionic adsorption onto the non-charged surface from solution

The net charge on one side of the interface must be balanced by an exactly equal net charge of opposite sign on the other side of the interface to maintain, overall electrical neutrality. An important aspect is the distribution of the counterions in the solution around a charged surface, since this determines the rate of change in electrical potential with distance from a charged surface.

In the diffuse double layer model (refer Fig 1.1), the ionic atmosphere on the solution side is supposed to consist of two regions:

1. a layer of strongly held counterions, adsorbed close to the charged surface on fixed sites due to strong electrostatic forces and
2. a diffuse layer of counterions, according to a balance between the electrical forces and those due to the random thermal motion.

According to this model the electrical potential drops rapidly in the fixed portion (Stern layer) of the double layer and more gradually in the diffuse portion. Mathematical treatment of the diffuse layer gives the effective thickness \(\kappa^{-1}\) of that layer. This is the distance from the charged surface into the solution within which the majority of electrical interactions are considered to occur. The effective thickness, often called the Debye screening length, is given by 1.1

\[
\kappa^{-1} = \left( \frac{\epsilon RT}{4\pi F^2 \sum \frac{C_i z_i^2}{2}} \right)^{\frac{1}{2}} \tag{1.1}
\]

where \(\epsilon\) is the static permittivity of a solution, \(R\) is the universal gas constant, \(T\) is the absolute temperature, \(F\) is the Faraday constant, \(C_i\) and \(z_i\) are the molar concentration and valency of any ion in the solution phase.

From equation 1.1 it is observed that \(\kappa^{-1}\) is inversely proportional to the valency of an ions and to the square root of its concentration in the solution phase.
Thus in the presence of an electrolyte, the electric effects have short range than in its absence (due to electrical double layer compression). For a 1:1 electrolyte at room temperature in aqueous solution, $\kappa^{-1}$ is 3 Å for 1000 mol m$^{-3}$, 10 Å for 100 mol m$^{-3}$, 30 Å for 10 mol m$^{-3}$, 100 Å for 1 mol m$^{-3}$ and 300 Å for 0.1 mol m$^{-3}$.

1.3 Properties of surfactant solutions

1.3.1 Adsorption at liquid gas and liquid-liquid interfaces

1.3.1.1 Gibbs adsorption equation and the surface excess concentration

The direct determination of surfactant adsorbed per unit area of liquid-gas interface is possible, but the methods employed are cumbersome and tedious [Clint, 1992]. A simple method involves surface tension measurement together with application of the Gibbs adsorption equation. The Gibbs adsorption equation in its most general form is given as

$$-d\gamma = \sum_i \Gamma_i d\mu_i$$

(1.2)

The equation relates the change in surface tension $\gamma$, with chemical potential $\mu$, for all species $i$, where $\Gamma_i$ is the number of moles of $i$ per unit area of the interface (surface excess concentration).

The surface excess concentration is defined as the excess material present in the surface phase due to adsorption over and above that which would be present if the bulk concentrations were continued right up to the interface.

For solutions consisting of a solvent 1 and a non-dissociating solute 2, the Gibbs equation is written as

$$-d\gamma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2$$

(1.3)

By convention the position of interface is such that the surface excess of solvent ($\Gamma_1$) is zero. At equilibrium between the interface and bulk phase concentrations, $d\mu_2 = R d\ln a_2$, where $a_2$ is the activity of the component in the bulk phase, $R$ is the gas constant & $T$ is the absolute temperature. For dilute surfactant solutions the activity of the solute ($a_2$) may be approximated to the concentration ($c_2$). Thus equation (1.3) takes the form

$$\Gamma_2 = -\left(\frac{1}{nRT}\right) \cdot \left(\frac{d\gamma}{d\ln c_2}\right)$$

(1.4)

This is the most commonly used form of the Gibbs equation. For solutions of
completely dissociated surfactant of the 1:1 type. The Gibbs adsorption is given as
\[
\Gamma_2 = -\left(\frac{1}{2RT}\right) \cdot \left(\frac{d\gamma}{dln c_2}\right)
\]  
(1.5)

where 2 is the value of prefactor \(n\). The prefactor, \(n\), represents the number of species at the interface whose concentration changes with the surfactant concentration. The value of \(n\) is 3 for a 2:1 or 1:2 surfactant. In dilute solutions of 1:1 ionic surfactant, with swamping amount of electrolyte, the value of \(n\) is 1 (same as the value of \(n\) for nonionic surfactants).

1.3.1.2 Method to estimate the surface excess concentration \(\Gamma_{max}\)

The surface excess concentration can be considered to be equal to surface concentration without significant error. The surface concentration of surfactant can be estimated from the surface tension or interfacial data by use of the appropriate form of Gibbs equation. A typical surface tension isotherm (\(\gamma - lnc_2\) plot) is shown in Fig 1.2.

In the region from A to B, the surface tension falls in a regular manner with a gradually increasing slope, corresponding to a regular increase in surface excess of component 2. The region B to C is essentially linear, indicating the slope of the curve is constant. A constant slope implies the surface is saturated and the surface concentration has reached its maximum value \(\Gamma_{max}\). The application of equation (1.4) from region B to C gives the value of \(\Gamma_{max}\).

The minimum area per head group at the interface \(a_{min}\) provide information on the degree of packing and orientation of the adsorbed surfactant at the interface. The \(a_{min}\) value is calculated from the relation (1.6)
\[
a_{min} = \frac{1}{A_v \Gamma_{max}}
\]  
(1.6)

where \(A_v\) is the Avogadro’s number.

1.3.1.3 The Szyszkowski equation

An alternate method of estimating the maximum surface concentration is by fitting the surface tension isotherm (from region A to C in Fig 1.2) with the Szyszkowski equation 1.7 [Clint, 1992].
\[
\gamma_0 - \gamma = \Pi = nRT \Gamma_{max} n(1 + Kc_2)
\]  
(1.7)

where \(\gamma_0\) and \(\gamma\) are the surface tension of water and surfactant solution respectively, \(\Pi\) is the surface pressure, \(\Gamma_{max}\) is the maximum surface excess concentration,
$c_2$ is the concentration of the surfactant solution, $R$ is the gas constant, $T$ is the absolute temperature, $n$ is the pre-factor and $K$ is the adsorption constant.

Szyuskowski equation is a correlation that relates the surface tension of surfactant solution with the bulk phase concentration [Rosen, 2004]. It is derived by combining the Langmuir adsorption isotherm with the Gibbs adsorption equation (1.4). The Langmuir adsorption equation (1.8) is given as

$$\frac{\Gamma_L}{\Gamma_{L,\text{max}}} = \frac{Kc_2}{1 + Kc_2} \quad (1.8)$$

where $\Gamma_L$ and $\Gamma_{L,\text{max}}$ are the adsorbed surface density and the maximum adsorbed surface density.

The basic assumption in the derivation is that the surface excess density ($\Gamma_2$) is approximated by the adsorbed surface density ($\Gamma_L$).

1.3.1.4 Effectiveness of adsorption at the interface

Effectiveness of surfactant adsorption is the maximum surface concentration attainable at the interface, irrespective of the bulk phase surfactant concentration [Rosen, 2004]. The surface concentration at surface saturation i.e $\Gamma_{\text{max}}$ is a useful measure of the effectiveness of adsorption. The effectiveness of adsorption is an important factor in applications involving foaming, wetting and emulsification. Tightly packed coherent interfacial films have different interfacial properties than loosely packed non coherent interfacial films.

1.3.1.5 Efficiency of adsorption at the interface

The bulk phase concentration of the surfactant needed to reduce the surface tension of water by 20 mN/m is taken as a measure of the efficiency of the surfactant ($C_{20}$) [Rosen, 2004]. It is observed that when the surface tension is reduced by 20 mN/m, the surface concentration is 84 - 99.9 % of its saturation value. Surfactant efficiency is conveniently estimated from the surface tension isotherm as illustrated in Fig 1.2. The lower the $C_{20}$ value, the more efficiently the surfactant adsorbs at the interface and more efficiently reduces surface or interfacial tension.

Factors that contribute to an increase in Efficiency of adsorption [Rosen, 2004] are:

1. Increase in the number of carbon atoms in the hydrophobic group
2. Straight alkyl chain in comparison to a branched alkyl chain containing the same number of carbon atoms.
3. A single hydrophilic group situated at the end of the hydrophobic group rather than at a central position.
4. A nonionic or zwitterionic hydrophilic group rather than an ionic one.
5. For ionic surfactants reduction in effective charge by a) use of more tightly bound (less hydrated) counterion, b) increase in ionic strength of the aqueous phase.

1.3.2 Surfactant solubility

In an aqueous solution when all available interfaces are saturated, the overall energy reduction may continue through other mechanisms [Tsuji, 1998]. Depending on the system composition, a surfactant can play different roles in terms of aggregation (formation of micelles, liquid crystals, bilayers, vesicles etc.) [Israelachvili, 1986]. The physical manifestation of one such mechanism is crystallisation or precipitation of surfactant from solution i.e bulk phase separation [Tsuji, 1998]. Even though surfactants have substantial solubility in water, this can change significantly with variations in tail length, head group nature, counterion valency and most importantly temperature.

1.3.2.1 Krafft point

As for most solutes the solubility increases with temperature. However for ionic surfactants, which are initially insoluble there is a temperature at which the solubility suddenly increases dramatically [Clint, 1992]. This is known as the Krafft temperature \( K_T \). It is the temperature at which the CMC curve meets the solubility curve [Moroi, 1992]. This is illustrated in Fig 1.4. Below \( K_T \) only monomeric surfactants can be in equilibrium with the crystalline surfactant. Above \( K_T \) micelles are formed to provide greater solubility.

The Krafft temperature is found to vary with counterion, alkyl chain length and chain structure. Knowledge of \( K_T \) is very crucial in many applications since below \( K_T \) solubility of the surfactant is too low to perform efficiently.

1.3.2.2 Cloud point

Micellar solutions of nonionic surfactants in water tend to become cloudy at a well defined temperature. This is referred to as the cloud point [Clint, 1992]. Above the cloud point, the system consist of an almost micelle free dilute solution (at a concentration equal to its CMC at that temperature) and a surfactant rich micellar phase. The separation is caused by a sharp increase in the aggregation number and decrease in intermicellar repulsions resulting form the decreased hydration of the oxyethylene oxygens in the polyoxyethylene hydrophilic groups with increase in temperature. This results in a density difference between the micelle rich and micelle poor phases. Since much larger particles are formed, the solution becomes
visibly turbid with large micelles efficiently scattering light. For polyoxyethylene nonionic surfactants with the same hydrophobe, increasing the ethylene oxide content results in increase in the cloud point, whereas increasing the hydrophobe chain length results in lowering the cloud point. Cloud point is also affected by the presence of salts and other surfactants.

1.3.3 Micellisation

In addition to forming oriented interfacial monolayers, surfactants tend to aggregate in solution provided the surfactant concentration is sufficiently high. These are typical clusters of 50-200 monomers, whose size and shape are governed by geometric and energetic considerations. Micelle formation occurs over a fairly sharp well defined range called as the critical micelle concentration (CMC). Above this concentration, additional surfactant forms the aggregate, whereas the concentration of the unassociated monomer remains fairly constant. Over exactly this range of concentration every measurable physical property that depends on the size or the number of particles in solution, suffers a discontinuity in its variation with concentration. Some typical results are illustrated in Fig 1.3.

1.3.3.1 Common methods to estimate CMC

Surface tension
A typical experiment involves measuring the surface tension as a function of surfactant concentration. Prior to micelle formation an increase in the surfactant concentration, decreases the surface tension due to adsorption of the surfactant to the surface. Beyond the CMC, the surface is saturated with the adsorbed surfactant molecules (Γ_{max} is reached) and any additional surfactant monomers added forms micelles. As a result the surface tension does not decrease further and attains a constant value (which is most often the case). Thus the break in the surface tension isotherm is inferred as the point at which micellisation begins. A typical surface tension isotherm is shown in Fig 1.2. The surface tension of surfactant solutions can be conveniently measured by the Du Nuoy ring or the Wilhelmy Plate method.

Conductivity
The method is suitable for ionic surfactants in the absence of added electrolyte. In the premicellar region, equivalent conductivity of surfactant solution plotted against the square root of concentration decreases slightly but linearly. The surfactant behaves like a conventional electrolyte. However above the CMC, there is a large decrease in equivalent conductivity of the surfactant solution, due to incom-
plete dissociation of the surfactant in micellar form. The micelles are less efficient carriers of charge than the equivalent number of fully dissociated monomers. The surfactant concentration at which the equivalent conductivity begins to fall rapidly is taken as the CMC of the surfactant. A typical plot is shown in Fig 1.3.

1.3.3.2 Mass action model of micellisation and the Corrin-Harkin plot

As per the mass action model, the micelles and monomers are considered to be in equilibrium [Moroi, 1992]. For a 1:1 ionic surfactant the mass action is represented as

$$NS + mG \rightleftharpoons S_N^{(1-\frac{m}{n})}$$

(1.9)

$S$ and $G$ are the surfactant monomer and counterion, $N$ is the aggregation number of the micelle, $m$ is the number of counterions bound to the micelle and $\frac{m}{n}$ is the counterion binding $N$ of the micelle.

Invoking law of mass action, with $K_M$ as the constant of micellisation,

$$K_M = \frac{[S_N^{(1-\frac{m}{n})}]}{[S]^N[G]^m}$$

(1.10)

$[S]$, $[G]$ and $[S_N^{(1-\frac{m}{n})}]$ are the surfactant, counterion and the micelle concentration respectively.

Applying Logarithm and rearranging we get

$$ln[S_N] = -\frac{m}{N}ln[G] - \frac{1}{N}lnK_M + \frac{1}{N}ln[S_N^{(1-\frac{m}{n})}]$$

(1.11)

Assuming that $N$ is large (>100) the last term on the right hand side of equation can be neglected. For the monomeric surfactant concentration taken as the CMC, the approximated expression is

$$lnCMC = -\frac{m}{N}ln\text{counterion concentration} - \frac{1}{N}lnK_M$$

(1.12)

The above equation predicts that logarithm of CMC will decrease linearly with the logarithm of counterion concentration which is in accordance with experimental findings. The slope of this curve is often interpreted as the counterion binding degree of the micelle which is the ratio of the number of counterions bound to the micelle to the aggregation number of the micelle [Moroi, 1992]. The plot of logarithm of CMC against the logarithm of counterion concentration is referred to as the Corrin-Harkin plot.

Equation 1.12 represents the simplest case of 1:1 ionic surfactant. For 2:1, 1:2 or other such types, an appropriate factor needs to be multiplied with the first
term on the right hand side of equation 1.12.

1.3.3.3 Counterion binding degree of the micelle

Aggregation of ionic amphiphiles is opposed by head group electrostatic repulsions which, however, are balanced to a great extent by adsorption of counterions at the micelle surface. It is commonly stated that about 60 - 70% of the counterions are bound to the micelles, where binding of counterions is described in terms of a continuous radial distribution function corresponding to a high counterion concentration close to the micelle and continuously decaying with increasing distance from the micelle. Thus there is no unambiguous distinction between bound and free counterions. The counterion binding degree defined as the ratio of the counterions and the amphiphile ions in a micelle, is not an experimentally well defined quantity, but varies with the experimental technique. The different techniques to estimate counterion binding degree can be classed as

1. Thermodynamic methods which involve the use of ion selective electrodes to monitor the the counterion concentration far away from the micelle. Another method to estimate counterion binding degree is from the slope of the Corrin-Harkin plot as discussed above.

2. Transport methods which monitor the amount of counterions moving along with the micelle as a kinetic entity and are exemplified by tracer self-diffusion measurements and the conductivity measurements.

3. Spectroscopic methods which monitor the amount of ions with its spectroscopic properties affected by the micelles. Examples are Nuclear Magnetic Resonance (NMR) chemical shifts or relaxation studies.

The above three methods are in qualitative agreement but not in quantitative agreement. The bound counterions reduce the net charge density at the micelle surface and allow the charged head groups to pack closely. The link between area of the head group and the counterion binding acts as a self regulating mechanism to keep the counterion binding degree constant in a given system [Clint, 1992]. When some counterions are removed from the surface, the head group area increases due to electrostatic repulsion, but the increase in net surface charge causes the counterions to condense. Thus the counterion binding degree of the micelle is found to vary little with surfactant concentration. Increased binding of a counterion to the micelle causes a decrease in the CMC of the surfactant [Rosen, 2004]. Counterion binding increases with increase in polarizability and valency of the ion and decreases with increase in its hydrated radius. More details are discussed below (refer 1.3.3.4, Counterion effects).
1.3.3.4 Factors affecting the CMC

The Hydrophobic group (tail)
For a homologous series of single chain surfactants the $CMC$ decreases logarithmically with the number of carbon atoms. The relation fits the Klevens equation [Rosen, 2004],

$$\log CMC = A - Bx$$  \hspace{1cm} (1.13)

Where, $A$ and $B$ are constants for a particular homologous series and temperature and $x$ is the number of carbon atoms in the hydrophobic chain. The value of $A$ depends on the nature and number of the hydrophilic group, while $B$ is a constant for all paraffin chain salts with a single ionic head group. Branching in the hydrophobe gives a higher $CMC$ in comparison to straight chain hydrophobe with same number of carbon atoms [Rosen, 2004]. Introduction of an aromatic group or a double bond in the hydrophobe produce noticeable changes in the $CMC$.

The hydrophilic group
Varying the nature of the hydrophilic group from ionic to nonionic decreases the $CMC$. For an ionic surfactant with straight chain hydrophobe having 12 carbon atoms the $CMC$ lies in the range of 1 $mol \cdot m^{-3}$, whereas for a nonionic surfactant with a similar hydrophobe the $CMC$ is in the range of 0.1 $mol \cdot m^{-3}$.

Counterion effects
In ionic surfactants micelle formation is related to the interactions between the solvent and the ionic head group. An increase in the degree of ion binding to the micelle will decrease the $CMC$. For a given hydrophobic tail and an anionic head group the $CMC$ decreases as $Li^+ > Na^+ > K^+ > Cs^+ > Ca^{2+}$. Similarly for a cationic surfactant the $CMC$ decreases as $F^- > Cl^- > Br^- > I^-$. In addition changing the counterion valency from monovalent to divalent or trivalent decreases the $CMC$ sharply.

Effect of added salts
The addition of an electrolyte substantially decreases the $CMC$ of ionic surfactants. The presence of salt partially screens the head group repulsions, thereby favouring micelle formation and lowering the $CMC$ [Clint, 1992]. Zwitterionic surfactants and nonionic surfactants show a weak effect in presence of electrolytes than the ionic surfactants.
Effect of temperature
The influence of temperature on the CMC of ionic surfactants is quite weak, however quite complex. The CMC of an ionic surfactant usually passes through a minimum when the temperature is varied from 0 - 70°C. The major effects of temperature on the surfactant solution are the Krafft point and the cloud point.

1.3.3.5 Structure of micelles and molecular packing

The shape of micelles produced in aqueous media is important in determining various solution properties such as viscosity, solubilisation capacity and cloud point. A theory of micelle structure based on the molecular geometry of surfactant molecules has been developed. The volume occupied by the hydrophobic tail \( V \), the length of the hydrophobic tail in the micelle core \( l \) and the minimum head group area at the micelle-solution interface \( a \) are used to calculate a critical packing parameter \( P \) \( (1.14) \) [Israelachvili, 1986]

\[ P = \frac{V}{la} \]  

(1.14)

From Tanford [Tabford, 1973] \( V \) and \( l \) are given as

\[ V = 27.4 + 26.9x \]  

(1.15)

\[ l \leq 1.5 + 1.265x \]  

(1.16)

where \( x \) is the number of carbon atoms in the chain

The expected aggregate structure in relation to the critical packing parameter is shown below

<table>
<thead>
<tr>
<th>( P )</th>
<th>Aggregate structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 1/3</td>
<td>Spherical or Ellipsoidal in aqueous media</td>
</tr>
<tr>
<td>1/3 - 1/2</td>
<td>Cylindrical or Rod shaped in aqueous media</td>
</tr>
<tr>
<td>1/2 - 1</td>
<td>Lamellar in aqueous media</td>
</tr>
<tr>
<td>&gt; 1</td>
<td>Inverse micelles in nonpolar media</td>
</tr>
</tbody>
</table>

1.3.3.6 CMC/\( C_{20} \) ratio

A convenient way of measuring the relative effects of some structural or micro-environmental factor on micellisation and on adsorption is to assess its effect on \( CMC/C_{20} \) [Rosen, 2004]. An increase in this ratio due to some factor, indicates that adsorption is facilitated over micellisation, a decrease indicates that micellisation is facilitated over adsorption. Thus this ratio gives an insight into the micellisation and adsorption processes.
1.4 Dynamic surface tension (DST)

Dynamic behaviour of surfactants can be investigated by dynamic surface tension (DST) measurements. The equilibrium surface tension of a surfactant solution is not achieved instantaneously [Ward and Tordai, 1940]. For example, when a fresh interface is formed, surfactant molecules must first diffuse from the bulk to the interface, and then adsorb, whilst also achieving the correct orientation. A freshly formed interface of a surfactant solution has a surface tension, very close to that of the solvent. Over a period of time, surface tension will decay to the equilibrium value, and this period of time can range from milliseconds to days depending on the surfactant type and concentration.

The dynamic surface tension is an important property as it governs many important industrial and biological processes [Porter, 1991]. For example, in the photographic industry the formulation of thin gelatin films requires high flow velocities, and hence DST needs to be monitored during the fabrication process to prevent film deformation and irregularities. DST is also important in the printing industry [Janule, 2005a] It is also of importance in agrochemicals where fast wettabiliy plays a role in the easy spreading of pesticides onto leaves [Stoeb et al., 1996]. DST also plays a crucial part in metal, paper and textile production. Coating is also one of the important application [Janule, 2005b]. One biological process where the control of DST is essential is in the lung [Chang et al., 2000], where low DST is necessary for effective functioning of the alveoli, and phospholipids are the main surface active ingredients. Recent advances in experimentation and theory, which are covered here, have been the stimuli for a resurgence in this area. In these cases, the dynamic surface tension (surface tension reduction as a function of time) of the surfactant is more important factor in determining the performance of the surfactant in the process than equilibrium surface tension.

The method which is used for DST measurement is maximum bubble pressure method as shown in Figure 1.5. The typical plot of the change in surface tension at with time contains four regions: an induction region (I), a rapid fall region (II), a meso-equilibrium region (III), and equilibrium (IV) as shown in Figure 1.6. Equation 1.17 fits the three dynamic regions (I-III).

\[ \gamma_t = \gamma_m + \frac{(\gamma_0 - \gamma_m)}{\left(1 + \left[\frac{t}{t^*}\right]^n\right)} \]  \hspace{1cm} (1.17)

Equation 1.17 can be converted to its logarithmic form to calculate the value of n and t*.

\[ \log(\gamma_0 - \gamma_t) - \log(\gamma_t - \gamma_m) = n \log t - n \log t^* \]  \hspace{1cm} (1.18)
The value of $t^*$ is the time required for $\gamma_t$ to reach half of the value between $\gamma_0$ and $\gamma_m$ and is related to the surfactant concentration. As the surfactant concentration increases, $t^*$ decreases. From equation 1.18, by differentiation, $t^*$ is also the time at which, at constant surfactant concentration, the rate of surface tension change with $\log t$ reaches its maximum value ($\text{max.} c$).

$$
\left( \frac{\delta \gamma_t}{\delta \log t} \right)_{\text{max.} c} = 0.576 \times n \times (\gamma_0 - \gamma_m)
$$

(1.19)

It has been suggested that $n$ is related to the difference between the energies of adsorption and desorption of the surfactant. The time, $t_f$, for induction period to end is an important factor in determining the surface tension as a function of time, since only when that period ends does the surface tension start to fall rapidly. The value of $t_f$ is related to the surface coverage of the air-aqueous solution interface and to the apparent diffusion coefficient, $D_{ap}$, of the surfactant.

1.5 Foaming

Absolutely pure liquids do not foam. Foam is produced when air or some other gas is introduced beneath the surface of a liquid that expands to enclose the gas within a film of liquid. Bubbles of gas introduced beneath the surface of an absolutely pure liquid rupture immediately on contacting each other or escape from the liquid as fast as the liquid can drain away from them. For foaming to occur, the presence of a solute capable of being adsorbed at the liquid gas interface is required. The presence of surfactants prevents the rupture of foam by adsorbing at the gas liquid interface or by reducing the liquid drainage from foam lamellae. Thus the effect of surfactant on foam formation and stabilisation would be an important property that need to be measured. Measurement of foam characteristics or properties such as volume and drainage in most of the cases are made, as a function of time, after foam is formed.

Ross and Miles developed a pouring method in 1941 [Ross and Miles, 1941], which later become ASTM standard in 1953. In Ross Miles method (see Figure 1.7), foam is obtained by pouring a constant volume of liquid onto a bed of same solution from a fixed distance at a given temperature. The collector tube is provided with water jacket to maintain constant temperature. Foam volume is recorded immediately after the last drop has fallen to get the foamability while foam volume measured as a function of a time gives an ideal of foam stability.
1.6 Mixed surfactant systems

Surfactant formulations used in household and commercial applications are generally blend of surfactants. Each surfactant may itself be a mixture of for example different chain lengths material but a blend here means two different surfactants carefully chosen so as to obtain optimum performance of the mixtures. There are many examples of binary mixtures of surfactants where the interaction between the two surfactants produces adsorption and micellisation properties quite different from the starting materials and many of these mixtures have commercial value. Commercial formulation relies on taking advantage of these interactions which may be cooperative (synergistic) or antagonistic. However prediction of the properties of strongly interacting systems which are most important in applications is not easy. In order to appreciate the difficulty in predicting the surface properties, it must be realised that the surface composition which determines the surface properties may be very different from the bulk. The interactions between the surfactant molecule at an interface are large since the molecules are closely packed.

Thermodynamics of mixed micelle and mixed adsorbed layer

The thermodynamics of mixed micelle formation can be treated using the phase separation model [Clint, 1992]. Consider a mixture of two pure surfactants, labelled as 1 & 2. Let $\alpha$ and $X_1$ denote the mole fraction of component 1 in the bulk and the micelle respectively. For a mixed micelle treated as an ideal mixture of its components and the activity coefficients of the surfactant monomers in the bulk taken as unity it can be shown that the monomer concentration of surfactant of 1, $C_1^m$ is given by:

$$C_1^m = X_1(CMC_1) \quad (1.20)$$

where $CMC_1$ is the critical micelle concentration of surfactant 1. A similar equation can be given for surfactant 2. For the condition that $X_1 + X_2 = 1$, one obtains the following relation

$$\frac{1}{CMC_{mix}} = \frac{\alpha}{C_1} + \frac{1 - \alpha}{C_2} \quad (1.21)$$

$CMC_{mix}$ is the critical micelle concentration of the mixture. Thus the $CMC$ of a mixture can be calculated from the $CMC$ values of its pure components. This is the equation of the ideal mixed micelle model based on the assumptions of the phase separation model.

However very few surfactant pairs fit this ideal mixed micelle model. In order
account for the nonideality Corkill introduced the Regular solution theory (RST) of bulk liquid mixtures. It was argued that since the micelle core is essentially liquid like, RST should be useful for mixed surfactant micelles. Introducing the activity coefficients $f_1$ and $f_2$ for the two surfactants within the mixed micelle in equation 1.21, the equation becomes

$$\frac{1}{CMC_{\text{mix}}} = \frac{\alpha}{f_1 CMC_1} + \frac{(1 - \alpha)}{f_2 CMC_2} \quad (1.22)$$

where the two activity coefficients for a binary system defined in terms of an interaction parameter ($\beta$) are given as

$$f_1 = \exp[\beta x_2^2] \quad (1.23)$$

$$f_2 = \exp[\beta x_1^2] \quad (1.24)$$

On solving further the interaction parameter $\beta$ is given by

$$\beta = \left( \frac{1}{X_2^2} \right) \frac{\alpha CMC_{\text{mix}}}{X_1 CMC_1} \quad (1.25)$$

The nonideality in the mixed adsorbed layer can be accounted in a similar way [Rosen, 2004]. An equation analogous to equation 1.22 can be written as

$$\frac{1}{CSC_{\text{mix}}} = \frac{\alpha}{f_1^{\gamma} CSC_1} + \frac{(1 - \alpha)}{f_2^{\gamma} CSC_2} \quad (1.26)$$

where $CSC_{\text{mix}}$, $CSC_1$ and $CSC_2$ are the concentrations of mixed and pure surfactants 1 & 2 needed to attain a certain surface tension value.

The two activity coefficients $f_1^{\gamma}$ and $f_2^{\gamma}$ of the the surfactants in the mixed adsorbed layer are given as

$$f_1^{\gamma} = \exp[\beta^{\gamma} x_2^{\gamma 2}] \quad (1.27)$$

$$f_2^{\gamma} = \exp[\beta^{\gamma} x_1^{\gamma 2}] \quad (1.28)$$

where $X_1^{\gamma}$, $X_2^{\gamma}$ and $\beta^{\gamma}$ are the mole fractions of the components and the interaction parameter in the mixed adsorbed layer at a surface tension $\gamma$ respectively. The interaction parameter $\beta^{\gamma}$ can be computed by an iterative solution of the following equation

$$\beta^{\gamma} = \left( \frac{1}{(X_2^{\gamma})^2} \right) \frac{\alpha CSC_{\text{mix}}}{X_1^{\gamma} CSC_1} \quad (1.29)$$

A positive interaction parameter implies a repulsive interaction whereas a nega-
tive interaction parameter implies cooperative or attractive interaction. Synergism in surface tension reduction efficiency is defined when the concentration of mixture needed to attain a certain surface pressure is less than the concentration of either of the pure components needed to attain the same surface pressure [Rosen, 2004]. Similarly synergism in mixed micelle formation is defined when the mixed micelle $CMC$ is lower than the pure component $CMC_s$ [Rosen, 2004].

1.7 Ecofriendly Surfactants

Copious amounts of surfactants is produced world wide every year. Most of the surfactants after utilization go down the drain and into the water treatment facilities for processing. Some surfactants used in common applications show little degradation by microbes [Hama et al., 1998]. Ultimately, the environmental impact of these surfactants from their synthesis process till their post application effects is a cause of considerable worry. Green or environmental chemistry involves the operation of set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and application of chemical products [Kidwai and R., 2005]. Due to the pressing need for environmentally benign product surfactants which are ecofriendly and derived from natural feedstock are of both scientific and practical interest. Keeping the above factors in mind, it is necessary to use renewable low-cost materials that are available in large quantities and to modify their molecular structures to improve their performance. The product should also have favourable ecotoxicological properties and minimum environmental impact [Rosen, 2004].

The surfactants obtained from sugar and oleochemical industries or derived from sea sources are well known [Roussel et al., 2005; Goursaud et al., 2008]. Green chemistry approach has a broader scope for handling most of the issues than the definition suggests [Sarkanen and Ludwig, 1971]. With the chemical waste and environmental related issues we also need to address the reduction in the amount of energy used in chemical processes [Goursaud et al., 2008]. The increasing awareness of effect of surfactants on the environment has caused increasing needs for more ecofriendly products. As a result, most chemical industries are moving towards producing surfactants which are derived from renewable resources [Moller et al., 2001]. Most of these surfactants are nonionic in nature that are manufactured entirely from natural, renewable resources such as plant oils [Yang et al., 2007]. These surfactants have great environmental compatibility and are highly biodegradable such as alkyl polyglucoside, treated natural fats and oils found in plants and sugar based surfactants [Haung and Verrall, 1997; Negm and Mohamed A., 2008; Negm and Zaki, 2008; Jurado et al., 2010].
One of the byproduct of oleochemistry is glycerol (triglyceride hydrolysis and methanalysis processes in biodiesel formation), with a growing contribution from industrial vegetable oils. Thus the use of glycerol, as well as vegetable oils, as starting materials for the manufacture of surfactants represents a convenient strategy for the development of surface active products. For example fatty acid esters of these polyols, called polyglycerol esters (PGE), have been developed leading to applications in cosmetic or food emulsifiers. In general, the preparation of PGE involves two subsequent steps, viz. (1) the polymerization of glycerol in the presence of small amount of alkali (base catalysis) and (2) esterification of the resulting polyglycerol as shown in Figure 1.8. The synthesis routes reported for the production of polyglycerol esters are usually achieved through (1) direct esterification of the polyol using either alkali [Lemke, 2002] or acid catalysts [Jakobson et al., 1995], (2) transesterification of the polyol with a triglyceride or a fatty acid methyl ester in the presence of a suitable alkaline catalyst [Marquez et al., 2004] or (3) Addition polymerization of glycerol to a fatty acid or to a fatty acid monoglyceride catalyzed by acids [Endo and Maruo, 2000].

The most commonly used cationic surfactants in household products are the alkyl ester ammonium salts that are used in fabric softeners (esterquats). These surfactants generally have undesirable effects on the environment, thus their use was recently reduced in many countries. The consumer demand for ecofriendly products, is causing manufacturers to focus on the production of cationic surfactants from alternative, less harmful raw materials. Glycine betaine, a not very expensive natural substance possessing a quaternary trimethylammonium moiety and a carboxylate function, constitutes a prime raw material for the preparation of biodegradable and biocompatible cationic surfactants. Within this context, novel glycine betaine esters and amides were recently produced from tropical oils (copra, palm kernel) or European oils (sunflower, rapeseed), conveniently, economically and with an environmentally acceptable process (no solvent, no waste) [Antoine et al., 2005].

The environment-friendly synthesis of glycine betaine esters was carried out through the direct esterification reaction between glycine betaine and fatty alcohols, preferably stearic and oleic alcohols, catalyzed by methanesulphonic acid without any solvent. Glycine betaine amides were prepared in two steps: first, glycine betaine reacts with n-butanol in the presence of methanesulphonic acid as catalyst. In the second step, the short butyl chain is replaced by a longer chain in an aminolysis reaction with fatty amines, particularly C18 stearic and oleic amines as shown in Figure 1.9.

In literature, [Koji et al., 2007] have reported synthesis of a cationic alkyl quaternary ammonium salt modified with glycerin at the head group, in order
to prevent precipitation when the cationic surfactant is mixed with anionic surfactant. The phase behavior of aqueous mixture of synthesized monoglycerol-cetyltrimethylammonium chloride (MGCA) and sodium octyl sulfate (SOS) was investigated. Similarly Moulik and coworkers have reported the interfacial and bulk behaviour of the amphiphiles hexadecylammonium bromide and its methyl and ethanolic head group analogues [Mitra and Moulik, 2010].
Solution phase

Distances from charged surface

0

Potential

Diffuse layer

Figure 1.1: Stern model of the electrical double layer.

Figure 1.2: A typical surface tension isotherm
Figure 1.3: Schematic representation of the concentration dependence of some physico-chemical properties around the CMC.
Figure 1.4: Schematic illustration of the Krafft temperature phenomena.
Figure 1.5: Schematic representation of dynamic surface tension measurement setup.

Figure 1.6: Typical plot of the change in surface tension with time.
Figure 1.7: Schematic representation of Ross Miles apparatus for foam measurement.
Figure 1.8: Synthesis of polyglycerol esters

Figure 1.9: Synthesis of glycine betaine fatty ester and amide