Chapter one

1.1 Introduction to Surfactants

Surfactants are molecules that can be considered to be made up of two parts, hydrophilic and hydrophobic portions. The hydrophilic-end is water-soluble and has usually a polar or ionic group (polar head). The hydrophobic-end is water-insoluble and is usually a long fatty or hydrocarbon (non-polar tail) chain. This dual functionality, hydrophobic and hydrophilic, provides the basis for characteristics useful in cleaner detergent formulation, including surface tension modification, emulsification, foam, and cloud-point determination. The simplest aggregate of these surfactant molecules is called a micelle, and the dispersion of the aggregates in water or oil is referred to as a micellar solution [1, 2]. When surfactants are dissolved in water then the hydrophilic part try to distort the intermolecular hydrogen bonding present between the water molecules and increase the free energy of the system whereas hydrophobic part try to keep aloof from water. Many excellent introductions to micelles are given by review articles [3-5]. A schematic representation of the general structure of a surfactant includes a hydrophilic and a hydrophobic portion is shown in the schematic below, and a micelle is shown in figure 1.1. An introduction to different types of surfactant molecules is given in the next section.

![Schematic of Surfactant and Micelle](image)

Figure: 1.1 schematic shown a general structure of a surfactant and micelle.
1.1.1 Surfactant Category

The Surfactants share in all the property of amphiphile, where the molecule is composed of hydrophilic and hydrophobic portion. The presence of hydrophilic portion makes surfactants slightly soluble in aqueous media. While the hydrophobic group is usually a long-chain hydrocarbon residue designated by the generic symbol, R. The surfactants are classified on the basis of the charge carried by the polar head group as:

(i) Cationic surfactants: The surface-active portion of molecule bears a positive charge for example, CTAB [C16 H33 N⁺ (CH₃)₃ Br⁻].

(ii) Anionic surfactants: The surface-active portion of molecule bears a negative charge for example, AOS [C₁₄H₂₇SO₃⁻ Na⁺].

(iii) Zwitterionic surfactants: The surface active portion of molecule bears both negative and positive charges for example, C₁₂ N (Me)₂(CH₂)₃ SO₃ [C₁₂ H₂₅ N (CH₃)₂(CH₂)₃SO₃].
(iv) Nonionic surfactants: The surface active portion bears no apparent ionic charge, where the head consists of a small molecular group; the hydrophilic part of the non-ionic surfactants molecule consists of a long chain. For example, TX-100 [4-(C$_8$H$_{17}$)C$_6$H$_4$(OCH$_2$CH$_2$)$_{10}$OH].

1.1.2 Critical micelle Concentration

When surfactant molecules are mixed in water it dissolves at very low concentration and nothing dramatic happens. When more and more surfactant molecules are added above a critical concentration known as CMC, it becomes energetically favorable for the molecules to form aggregates such that the part that has the water liking part is in contact with water. The water hating parts bundle up together. Critical micelle concentration (CMC) is a measure of surfactant efficiency. A lower CMC indicates less surfactant is needed to saturate interfaces and form micelles. Typical CMC values are less than 1% by weight. There are other factors that affect the CMC value in aqueous solution like:
(i) Structure of the Surfactant

In general, the CMC in aqueous media decreases with increase of number of carbon atoms in the hydrophobic group to about 16. This also depends on the type of hydrocarbon chain (i.e. linear or branched) where the carbon atoms on the branches appear to have about one-half the effect of carbon atoms on a straight chain [6]. The hydrophilic groups effect the value of CMC, where the ionic head group have much higher CMC than nonionic head group containing equivalent hydrophobic group. The zwitterionic head group appears to have about the same CMC as ionics with same number of carbon atoms in the hydrophobic group. Table 1.1 shows structure and CMC values of typical amphiphilic surfactants [7].

(ii) Electrolyte

The presence of added electrolyte in the aqueous solution causes a decrease in the CMC because of the decrease in the thickness of the additional electrolyte layer and the consequent decreased electrical repulsion between these in the micelle.

(iii) Organic additive

The presence of various organic additives in the aqueous solution, where addition of small amounts of organic materials may produce marked change in the CMC. A number of authors have reported the effects of added organic materials on the CMC of ionic surfactants [8-10]. From some of those studies it is evident that the effects, while small, can be experimentally significant. The presence of organic materials will result in a reduction in the dielectric constant of the solvent mixture. This effect would tend to decrease the CMC of ionic surfactants, due to their lower solubility and reduced repulsion between adjacent head group at the micellar surface. The net effect on the CMC will therefore depend on the relative magnitudes of the opposing trends.
### TABLE 1.1 Typical Amphiphilic Structure

<table>
<thead>
<tr>
<th>Types and Class</th>
<th>Structure</th>
<th>Amphiphile</th>
<th>Symbol</th>
<th>CMCM(T°C)(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionics (sodium alkysulfate)</td>
<td>( \text{F}<em>n \text{H}</em>{2n+1} \text{SO}_4 \text{Na} )</td>
<td>Sodium octylsulfate</td>
<td>( \text{C}_n \text{SO}_4 \text{Na} )</td>
<td>( 1.33 \times 10^7 )</td>
</tr>
<tr>
<td></td>
<td>( \text{F}<em>n \text{H}</em>{2n+1} \text{SO}_4 \text{Na} )</td>
<td>Sodium decaylsulfate</td>
<td>( \text{C}_{10} \text{SO}_4 \text{Na} )</td>
<td>( 3.3 \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>( \text{F}<em>n \text{H}</em>{2n+1} \text{SO}_4 \text{Na} )</td>
<td>Sodium dedecylsulfate</td>
<td>( \text{C}_{12} \text{SO}_4 \text{Na} ) (SDS)</td>
<td>( 8.1 \times 10^2 )</td>
</tr>
<tr>
<td>Anionics (Sodium Alkylcarboxylate)</td>
<td>( \text{C}<em>n \text{H}</em>{2n+1} \text{O}_2 \text{Na} )</td>
<td>Sodium dedecanoate</td>
<td>( \text{C}_{11} \text{SO}_4 \text{Na} )</td>
<td>( 2.5 \times 10^3 )</td>
</tr>
<tr>
<td>Sodium 1,4 dialkyl-3- Sulfonate-succinate</td>
<td>((\text{CH}_2 \text{CH}_2)_2 - \text{CH}^- (\text{CH}_2)_2 \text{O} = \text{O} )</td>
<td>Aerosol OT</td>
<td>AOT</td>
<td>( 6.8 \times 10^4 )</td>
</tr>
<tr>
<td>Cationics</td>
<td>( \text{C}<em>{12} \text{H}</em>{25} \text{N} (\text{Me})_3 \text{Br} )</td>
<td>Dodecyl trimethyl ammonium bromide</td>
<td>( \text{C}_{12} \text{N} (\text{Me})_3 \text{Br} )</td>
<td>( 1.5 \times 10^2 )</td>
</tr>
<tr>
<td>Ammonium bromide</td>
<td>( \text{C}<em>{16} \text{H}</em>{33} \text{N} (\text{Me})_3 \text{Br} )</td>
<td>Hexadecyl trimethyl ammonium bromide</td>
<td>( \text{C}_{16} \text{N} (\text{Me})_3 \text{Br} ) CTAB</td>
<td>( 9.2 \times 10^4 )</td>
</tr>
<tr>
<td>Dialkyl dimethyl ammonium bromide</td>
<td>( \text{C}<em>{12} \text{H}</em>{29} \text{N} (\text{Me})_2 \text{Br} )</td>
<td>Didecyl dimethyl ammonium bromide</td>
<td>( \text{C}_{12} \text{N} (\text{Me})_2 \text{Br} ) (DDAB)</td>
<td>( )</td>
</tr>
<tr>
<td>Dialkyl dimethyl ammonium acetate</td>
<td>( \text{C}<em>{12} \text{H}</em>{29} \text{N} (\text{Me})_2 \text{CH}_3 \text{CO}_2 )</td>
<td>Dihexadecyl dimethyl ammonium acetate</td>
<td>( \text{C}_{12} \text{N} (\text{Me})_2 \text{CH}_3 \text{CO}_2 ) (DHDAA)</td>
<td>( )</td>
</tr>
<tr>
<td>Zwitterionic</td>
<td>( \text{CH}_2 \text{O} - \text{C} - \text{C}<em>n \text{H}</em>{2n-1} )</td>
<td>Dimyristoyl-lecithin(n=140DMC)</td>
<td>Dimyristoyl-lecithin(n=140DMC)</td>
<td>( 5 \times 10^{-6}(41°C) )</td>
</tr>
<tr>
<td>Dialkyl phosphatidylcholine</td>
<td>( \text{CH}_2 \text{O} - \text{C} - \text{C}<em>n \text{H}</em>{2n-1} )</td>
<td>Dipalmitoyl-lecithin(n=160DPPC)</td>
<td>Dipalmitoyl-lecithin(n=160DPPC)</td>
<td>( 5 \times 10^{-6}(41°C) )</td>
</tr>
<tr>
<td>Alkyl dimethylpropane sulfinate</td>
<td>( \text{C}<em>n \text{H}</em>{2n} \text{N} (\text{Me})_2 (\text{CH}_2)_2 \text{SO}_2 )</td>
<td>Deducane-dimethyl-propanesulfinate</td>
<td>( )</td>
<td>( 3.6 \times 10^{-6}(30°C) )</td>
</tr>
<tr>
<td>Nonionic</td>
<td>( \text{C}<em>{10} \text{H}</em>{21} \text{(CH}_2)\text{CH}_3 \text{OH} )</td>
<td>Dedecylmethlylamine oxide</td>
<td>( \text{C}_{10} \text{Me} \text{NO} )</td>
<td>( 1.9 \times 10^2 )</td>
</tr>
<tr>
<td>Alkylylamine oxide</td>
<td>( \text{C}<em>{10} \text{H}</em>{21} \text{(CH}_2)\text{NO} )</td>
<td>Dedecylmethlylamine oxide</td>
<td>( \text{C}_{10} \text{Me} \text{NO} )</td>
<td>( 1.9 \times 10^2 )</td>
</tr>
<tr>
<td>Alkyglycoside</td>
<td>( \text{C}<em>{10} \text{H}</em>{21} \text{C}_6 \text{H}_11 )</td>
<td>B-deglycoside</td>
<td>( )</td>
<td>( 2.2 \times 10^4 )</td>
</tr>
<tr>
<td>Triton-X100</td>
<td>( \text{C}<em>{10} \text{H}</em>{21} \text{(CH}_2)\text{CH}_3 \text{OH} )</td>
<td>( )</td>
<td>( )</td>
<td>( 2.1 \times 10^8 )</td>
</tr>
</tbody>
</table>

(a) The naming of organic compounds is often a source of considerable frustration to the uninitiated. To add to the confusion, two or three names are used interchangeably for many alkyl chains. (b) \( 25°C \) unless otherwise noted.
(iv) Temperature.

The CMC of surfactants in aqueous medium is affected by the temperature though it is not clear how. Increase in temperature causes disruption of the structured water surrounding the hydrophobic group. This effectively disfavors micellization. Another affect that disfavors micellization with increasing temperature causes decreased hydration of the hydrophilic group. The values of CMC over a particular temperature range increase or decrease depending on these two opposing effects. The CMC of the most ionic surfactants passes through a minimum as the temperature is varied from about 0 through 60-70 °C [11]. Nonionic and Zwitterionic materials are not quite so predictable, although is has been found that some nonionic surfactant reach a CMC minimum around 50 °C [12].

1.1.3 Micellar structure and Shape.

Hartely proposed micelles are spherical with charged groups sited at the micellar surface; he suggested that the structure should be composed of 50-100 molecules and that association should occur over a relatively narrow concentration range [13]. Mc Bain proposed that spherical and lamellar forms coexist [14]. Harkins et al suggested the sandwich or lamellar model [15]. Debyc and Anacker proposed that micelles are rod-shaped rather than spherical or disk like [16]. In 1956 Reich established from the view point of entropy [17] the spherical micelle model by Hartely and the spherical form is now generally accepted as a approximating the actual structure with an interior region containing the hydrophobic groups of the surfactant molecules of radius approximately equal to the length of a fully extended hydrophobic group, surrounded by another region containing the hydrated hydrophilic group and bound water. In ionic micelles, a region that contains the ionic head groups, the Stern layer,
surrounds the interior region. Somewhat more than one-half of the counterions are associated with the micelle. The remaining counterions are contained in the Gouy-Champman portion, which further extends to the interior to the aqueous phase as shown in figure 1.2. Spatial variation of double layer potential \( V(r) \) is shown in figure 1.3, where over a very small distance the potential varies as \( 1/r \) due the presence of two opposite types of charges and then in Gouy-Champman region it falls exponentially. In hydrocarbon medium, the structure of the micelle is similar but reversed. The hydrophilic heads settle in the interior and outer region comprises the hydrophobic groups. Dipole-dipole interactions hold the hydrophilic heads together in the core [18]. However, as the ion concentration is increased the shape of the ionic micelles changes in the sequence spherical-cylindrical-hexagonal-lamellar as illustrated in figure 1.2 [19-23]. For nonionic micelles, on the other hand, the shape seems to change from spherical directly to lamellar with increasing concentration [24, 25].

Figure 1.2: Diagram of an anionic micelle with different layers.
Figure 1.3: The potential in Stern region, which varies as $1/r$ and in the Gouy-Chapmann region it falls exponentially.

Figure 1.4: Change in micelle shape and structure with changing surfactant concentration.
1.2 Polymers

Polymer is a Greek word meaning many (poly) parts (mer). These are basically large molecules composed of many small molecules. Due to their largeness in size; they are sometimes called as macromolecules. The molecular weight of an ordinary polymer is 5 to 10 thousand Daltons and can be as high as several millions Daltons. In comparison to this the molecular weight of a low molecular weight compound will not be more than few hundred Daltons. To contrast the difference, the molecular weight of NaCl is 58.5 and that of methane, CH₄ is 16. Whereas a polymer can be have molecular weight as high as several hundred thousands. A molecule with a only a few repeating units (but not large enough to be called a polymer) is called an oligomer, the physical properties of which varies with the addition or removal of one or a few constitutional repeating units from its molecules. The process by which a monomer is converted to a polymer is called polymerization. A polymer can have one, two and sometimes three or more types of monomers. Polymers are classified into two groups, one is natural polymers obtained from natural products such as natural rubber, wool, cellulose, collagen etc. The second group is called synthesized polymer such as plastics, teflon, nylon etc. If the backbone of the polymer is made up of carbon atoms, then the polymer is called as an organic polymer otherwise it is called an inorganic polymer. Some of the natural organic polymers exhibit some biological activity and they are called as biopolymer. If the backbone of a polymer contains a single type of monomer, then it is called as homopolymers. If it contains more than one type of monomers it is called as copolymer. If two types of monomers combine alternatively, then are called as alternating polymer. When they combine randomly in a polymer it is called a random copolymer. If in a copolymer a group of monomers of another type then the polymer is called as a block copolymer. Whereas
if the blocks of one of the monomers are joined to the backbone of a polymer consisting of different type of monomers, the polymer is called as a grafted copolymer. The structures of all these polymers are shown in the figure 1.5

![Image showing different types of polymers](image)

Figure 1.5: Schematic representation of structure of polymer: random polymer; alternating Copolymers block copolymer; graft copolymer

### 1.2.1 Polymer Formation

The monomers should be at least bi-functional (i.e. the number of available binding sites, they should have at least two reactive sides). A bi-functional monomer leads to formation of a linear polymer. On the other hand if some of the monomers will have functionality more than two, the polymer will be branched polymer. Under certain special conditions a branched polymer can form cross-linked or network polymer. Different types of polymers are sketched in the figure 1.6.
A synthetic polymer can be made in the laboratory from monomers by one of the two methods called poly condensation and poly addition. In the case of poly condensation in each step of polymerization a low molecular weight substance will be liberated. Depending on the degree of polymerization, polymers of different molecular weight are produced in a polymer reaction. Whereas in the case of poly addition no such low molecular weight substances are liberated.

1.3 Proteins

The name protein is derived from a Greek word proteios meaning of prime importance. Most of the solid matter from which living organism are made has a remarkably uniform composition. In living organisms only a few elements are present and they occur in proportion 54% of carbon, 7% of hydrogen, 16% of nitrogen, 22% of oxygen and 1% of sulphur. These are of great importance in the construction and chemical activity of living organism and are called as proteins. A protein is a linear
chain whose backbone is made up of succession of amino-acid monomers whose basic composition is shown in figure 1.7.

![Figure 1.7: Single amino acid molecule.](image)

Where COOH is the carboxyl group, NH₂ is the amine group and R can contain, apart from C and H (Hydro-carbon), other atoms like O, S, N, etc. There are twenty types of amino acids, which differ in their side groups. The smallest and simplest one being glycine, where R=H. Under the normal physiological conditions the amino acids exist in doubly ionized form. In this case the acidic carboxyl group can lose a proton and the basic amino groups gain a proton to form a dipolar ion or zwitterions as shown in figure 1.8.

![Figure 1.8: Transition of amino acid from nonionic to zwitterionic form.](image)
Proteins are formed by polycondensation of amino acids. In each step of condensation a peptide bond is formed by the loss of one water molecule. When two amino acids combine this way, they form a single peptide bond and the resulting product is a dipeptide shown in figure 1.9. In this way, when 3 amino acids combine together, they form two peptide bonds and the resulting product is a tri-peptide. A tetra-peptide, a penta-peptide can be formed out of 4 amino acids, 5 amino acids respectively. When the number of peptide bond is less than 100 it is generally called as a polypeptide and when it is more than 100, it is called as a protein, although the demarcation is not very sharp. The characteristic molecular masses of individual chains in proteins are of order of 20,000, which corresponds to 150-180 amino acid residues (the average molecular weight of an amino acid residue is 120) whereas for proteins it can be much larger.

![Figure 1.9: Schematic of formation of peptide bond through polycondensation.](image)
Therefore proteins are made up of many amino acids in which they are bound together by a peptide linkage forming between the amino groups of one amino acid to the carboxyl group of another.

1.4 Gelatin

Gelatin has existence in nature can be derived from a parent protein called collagen, by one of the many ways involving the destruction of secondary structure of the collagen, mostly this is achieved by both chemical and thermal treatments. This is the reason why it is sometimes called, as denatured or disorganized collagen comprises of 30% of the total organic matter in mammals and 60% of the total protein contents. Most of the collagen is localized in major tissues like skin, bones, and tendons, but collagen fibers pervade almost every organ and tissue. Due to its wide spread distribution and functions, fibers in various tissues are organized macroscopically in different ways, are produced by different types of cells and are intimately associated with varying types and amounts of other substance.

Gelatin is the only degraded proteins that have excited so much of scientific interest. Originally because of its use in food (like: salads, candies, bakery goods, etc), pharmaceutical and cosmetics industries. In aqueous solution at sufficiently high temperature the peptide chains take up random configuration. This is analogous to the behavior of synthetic linear chain high polymers. So these allow us to examine the structure and behavior of gelatin from the point of view of the theories developed to treat such high polymer systems. Another interesting area of study is the sol-gel transition in gelatin gel. From this one can derive information about explicit nature of phase transition occurring at gelation point, properties of physical gel, scaling relation, etc. There are many good review articles on this topic 'gel' [26-30] and all
of them tried to answer the same century old question "what is gel?" "What it constitutes of?" Despite this, scientists are yet to find a common answer to this. The reason for this being scientists and researchers working in different discipline try to bring in more and more materials into this according to their own convenience and define it accordingly. In this process they introduced a number of related terms, i.e., weak gel, quasi-gel, temporary-gel. Pseudo -gel, hetero-gel, iso-gel, micro-gel, nano-gel, xero-gel, etc. In a simplest way a gel is defined as a cross-linked polymer network swollen in a liquid medium. The properties depend very strongly on the interaction of two components. In a gel the liquid prevents the polymer network from collapsing into a compact mass and the network in turn retains the liquid.

Gel resulting from an outstanding variety of mechanism can be broadly divided into two categories. First is chemical gel and the second is physical gel. A chemical gel is formed by chemical reaction (like: co polymerization, poly condensation, vulcanization) leading to formation of a branched network (cross-linked network) made up linear, flexible chains attached by covalent bonds and surrounded by large quantity of solvents. These are some times called as strong gels. The network can be called the "fishing net gels". On the other hand a physical gel can be formed by the formation of weak bonds like hydrogen bonds, vander waals forces or hydrophobic and ionic interactions. This is the reason why they are sometimes termed as "weak gel Gelatin gel, Agarose gel etc. Probably the originator of the term gel is Thomas Grahm [31]. He proposed a different class of substances according to there ' diffusive power': the colloidal substances are slowly diffusing substances, which are held in solution by "feeble forces". Following Grahm, a rich literature developed in the colloid field.
Then this idea about gel arose progressively that a gel is a continuous solid state extending throughout the liquid and forming a framework for the liquid. But it was not very clear whether the framework was purely amorphous or purely crystalline. Thereafter, several definitions of gels followed. Herman defined a gel as: A coherent system of at least two components, which exhibit mechanical properties characteristic of a solid, where both the dispersed component and the dispersed medium extends itself throughout the whole system [26]. His definitions of gels exclude the one component system such as fully cross-linked linear polymer. So, his definition was not in agreement with the Flory – Stockmayer [32]. Gelation theory of Djabourov [28] propose putting a limiting value of storage modulus as a measure of gel-rigidity:

$$E = \lim_{\omega \to 0} \frac{G'(\omega)}{\omega}$$

Where: $\omega$ is the angular frequency and $E$ is termed as relaxation shear modulus. Almdal et al. [30] also suggested that solid-like gels are characterized by the absence of an equilibrium modulus, by a storage modulus, $G'(\omega)$ which exhibits a pronounced plateau extending to times at least to an order of seconds and by a loss modulus, $G''(\omega)$ which is considerably smaller than the storage modulus in the plateau region. An equilibrium shear modulus develops at the onset of gelation.

Let's discuss the structure of a collagen and what it consists of? Collagen, which is unique among proteins, has an amino-acid composition that comprises mainly of hydroxyproline, and is extraordinarily rich in glycine and proline as shown in figure 1.10. It has very low sulphur content. Every third element of collagen is a glycine residue (27%). And an important amount of amino-acid proline and hydroxy proline residue (25%, of the total) is present in collagen protein. Although the chemical
composition of collagen is not unique, a typical sequence of collagen protein is given by

\[ -(\text{Gly} - \text{Pro} - X) - \text{ OR } -(\text{Gly} - X - \text{Hypro}) - \]

Where “X” represents different amino-acid. The presence of these rings in proline and hydroxyl-proline gives an enhanced localized rigidity to the chain The side groups of the amino-acid also play an important role in the stability of proteins. Some of these have polar groups (like: OH, CO, NH₂, etc.) which are likely to interact with water molecules and establish hydrogen bonds. There are also polar charged groups (like: NH₃⁺, COO⁻, etc.) in variable amounts. The portion of charged NH₃⁺ or COO⁻ groups are also hydrophilic. Hydrophobic groups (such as those of proline) are also encountered. The conformation that a protein adopts when dissolved in solution (generally aqueous solution) is a direct consequence of the balance between hydrophilic and hydrophobic interaction, which in turn results from molecular composition.

\[ \text{Gly} \rightarrow \text{Glycine} \rightarrow H - C - COOH \]

\[ \text{Pro} \rightarrow \text{Proline} \rightarrow \text{Proline} \]

\[ \text{Hypro} \rightarrow \text{Hydroxyproline} \]

Figure 1.10: Chemical structure of Glycine, Proline and Hydroxy-proline.
The definitive property of all collagen is the triple helix, a unique protein conformation that is a coiled coil of three polypeptide subunits, or α chains. Each α chain twists in a left-handed helix with three residues per turn, and the three chains are wound together in a right-handed super helix to form a rod-like molecule about 1.4nm in diameter. In common collagens, the length of each collagen strand (α chain) is 1050 residues (primary structure) and the molecule is typically 200nm long. The pitch of the helix is approximately 0.9nm. The torsion of the chain is such that (C = O) and (N – H) groups attached on the main chain are oriented perpendicularly to its axis and are not in position to establish intra-chain hydrogen bond to stabilize the helix. So the question arises, how else could the helix be stabilized? The answer for collagen is the triple helix. The three strands are wrapped together into a right-handed super helix, with pitch roughly 10 times longer (~ 8.6nm). The presence of “Gly” is required to allow the three chains come closer to each other, while “pro” and “Hypro” residues enhanced the rigidity. The gradual gentle right-handed twist of the individual strands allows the side groups of various sizes to come into the structure. Collagen is probably the only polypeptide that forms a triple helical structure in hydrogen bond friendly environment.

The collagen triple-helix is stabilized by inter-chain hydrogen bonds, which are perpendicular to the chain axis. The hydrogen bonds can be of several types, either directly between (C = O) and (N – H) between two adjacent backbones or via water molecules situated in interstitial positions inside triple-helix. The overall length of the rod of triple-helix is around 200nm. The rods are arranged in parallel rows, to build the fibers, which are attached by additional covalent bonds located at both ends of the rods. These bonds make the collagen fibers insoluble.
1.5 Binding of Surfactants to Proteins and gel

Contacts between surfactants and proteins are extremely frequent in our daily lives. The effects of surfactants on polymer are of special interest particularly in pharmaceutical or cosmetic applications. The properties of proteins, enzymes and membranes are dramatically changed when these come closer to surfactants specifically ionic surfactants. When a surfactant is added to polymer then surfactant monomers try to bind to the charged sites of polymer, if the polymer has charged sites or to the uncharged sites of polymer through hydrophobic interactions. Increasing the concentration of surfactants causes distortion or smearing out of the weak bonds like inter and intra-molecular hydrogen bonding of polymer, which cause the uncoiling of the polymer chain. For the globular proteins, it causes denaturation. When the concentration of surfactant increases, first monomer concentration increases and these bind to the charged sites of polymer. When this type of binding is saturated, these start aggregating at a concentration called, Critical Aggregation Concentration” (CAC) < CMC Then at some particular concentration, it starts micellization (sharp decrease in surface tension) as shown in figure 1.11, keeping their head groups wrapped around by polymer chains or micellized over the neutral sites of polymer. This model is called “Necklace bead model” (sketched clearly) in figure 1.12.

Surfactants are known to interact with polymer gels with specificity. The chemical and physical polymer gels interact differently with ionic and neutral surfactants. In physical gels, a three-dimensional interconnected network of polymer chains is formed in the dispersion medium, which is held together by intermolecular hydrogen bonding. The physical gels achieve solution stability through an array of possible secondary forces, like hydrogen bonds, van der Waal forces, dipolar interactions and
hydrophobic interactions etc. In chemical gels the network mainly comprises primary forces (covalent bounds). The fluidity and elasticity of such gels become a matter of time scales of the observations relative to the lability of these interactions, which are amenable to modifications through selective binding to micelles among other possibilities [33].

Figure 1.11: Determination of the critical micelle formation concentration
Figure 1.12: Necklace bead model of polymer-surfactant complex where (A) polymer wraps around micelle and (B) polymer-surfactant complex where micelle formed around the hydrophobic side of the polymer.

1.6 References


