Chapter 1

General Introduction

1. Introduction

1.1 Soft Matter Research:

The pace of worldwide research in the areas like macromolecular and association colloids, emulsions and microemulsions, gels, membranes, liquid crystals, nano particles etc. in recent years is amazing. This has led to the emergence of "soft matter" science and technology as a distinct interdisciplinary area of Chemistry, Physics, Life Sciences, Chemical Engineering, Pharmacy and Material Science. The study of soft matter aims at identification of molecules that form specific structures in a particular environment and probing into the causes that induce the structures formation, understanding of the specific functional aspects of the structures formed, designing specific structure with desired properties of the structures formed. Biological systems provide ample examples of structure and compartment formation. A clear understanding may help drug design, encapsulation, targeting and delivery. Natural process may be conveniently mimicked to advantage for applications in pharmacy, medicine, agriculture and industry.

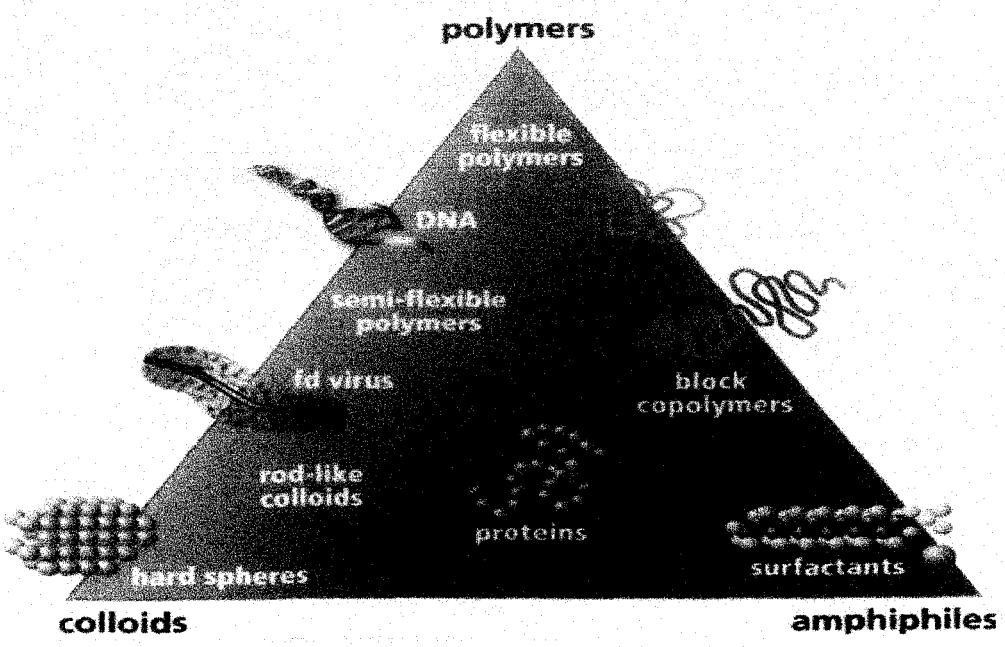


Figure1.1: The "soft -matter triangle": it encompasses a broad, continuous range of materials, from colloidal suspensions of particles to flexible long-chain polymer molecules and amphiphilic or soap-like, systems. Many biological systems such as proteins, DNA and virus have the characteristics of all these soft-matter types.

1.2 Self-Assembly of Amphiphilic Molecules

Amphiphilic molecules have been the realm of interest in chemistry for over a hundred years with attention not only in pure science but also in their wide applications to industry. Self-assembly is a spontaneous organization of molecules driven by noncovalent interactions into stable aggregates. Self-assembly is also well recognized in biological systems, e.g., lipid bilayers, the DNA duplex, and tertiary and quaternary structure of proteins. The process of spontaneous aggregation of single molecules in solution into larger structures with a certain order is also an important phenomenon in every-day-life as well as in science. The best known example of aggregation in every-day-life is the formation of micelles by detergent molecules. The most important type of aggregation, which is essential to life, is the formation of the lipid bilayer membrane by phospholipids. It has inspired chemists and physicists to study and mimic this and other types of aggregates [1]. Aggregation of molecules often occurs at the borderline of solubility. An important molecular property in this respect is polarity, for which solubility follows the rule 'like dissolves like'. Polar (hydrophilic) compounds are well soluble in polar solvents, e.g. salt in water, and the same goes for apolar (hydrophobic) compounds and solvents, e.g. vitamin E in oil. Furthermore, polar compounds are insoluble in apolar solvents and vice versa. Things become more interesting when a compound has amphiphilic properties, i.e. when it contains a polar as well as an apolar part. The polar part is called "head" and the apolar part usually a long chain hydrocarbon is called "tail" (see Figure 1.2). These compounds are most comfortable in a situation when each part is located in an appropriate environment, which is only possible at the interface between two media. Therefore, amphiphilic compounds are also called surface-active agents, or in short, surfactants [2]. The head group may be anionic, cationic or nonionic and accordingly the surfactants are classified as anionic, cationic or nonionic.

Figure 1.2: Schematic representation of an amphiphile.

There are some surface active amphiphilic molecules that contain both anionic and cationic centers at the head group. These are called zwitterionic surfactants. Surfactants can also have two hydrocarbon chains attached to a polar head and are called double chain surfactants. On the other hand, surfactants containing two hydrophobic and two hydrophilic groups are called "gemini" surfactants. Amphiphilic molecules can also have two head groups (both anionic, both cationic or one anionic and the other cationic) joined by hydrophobic spacer [3]. These types of molecules are termed "bola-amphiphiles" commonly known as "bolaforms". Surface activity of these molecules depends on both the hydrocarbon chain length and the nature of head group(s). Amphiphiles with longer hydrocarbon chains are found to be more surface-active compared to those having shorter hydrocarbon tail [4]. It is observed that amphiphiles with fluorocarbon chain are more surface-active than those with hydrocarbon chain. This is because the fluorocarbon chain is more hydrophobic than hydrocarbon chain [5].

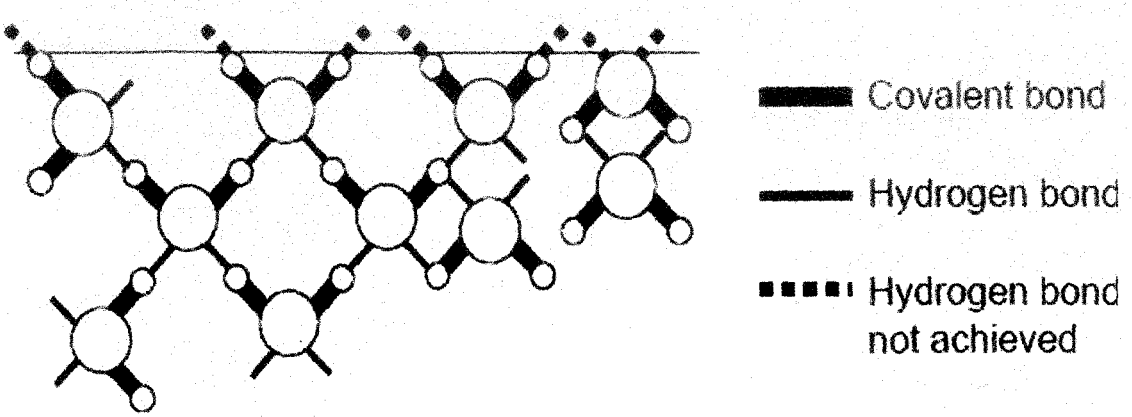


Figure 1.3: Water molecules at the liquid-air interface

Water is a very cohesive liquid due to the formation of a 3-dimensional hydrogen bond network (Figure 1.3) in addition to attractive van der Waals interactions.

This induces that the amount of work required to expand the interface air-water, characterized by the surface tension, is relatively high (72.6 mNm^{-1}, for pure water at 20°C). When surfactants are added to water, they adsorb at the water-air interface, which actually arises from their dualistic character. In aqueous solution the hydrophobic chain interacts weakly with the water molecules, whereas the hydrophilic head interacts strongly via dipole or ion-dipole interactions. It is this strong interaction that renders the surfactant soluble in water. However, the cooperative action of dispersion and hydrogen bonding between the water molecules tends to squeeze the surfactant chain out of the water (hence, these chains are referred to as hydrophobic). Therefore, surfactants tend to accumulate at the surface, which allows lowering the free energy of the phase boundary, i.e. the surface tension.

1.3 Structure and Shape of Aggregates: The Packing Parameter

The concept of molecular packing parameter has been widely cited in chemistry, physics, and biology literature because it allows a simple and intuitive insight into the self-assembly phenomenon [6]. The packing parameter approach permits indeed to relate the shape of the surfactant monomer to the aggregate morphology [7-9].

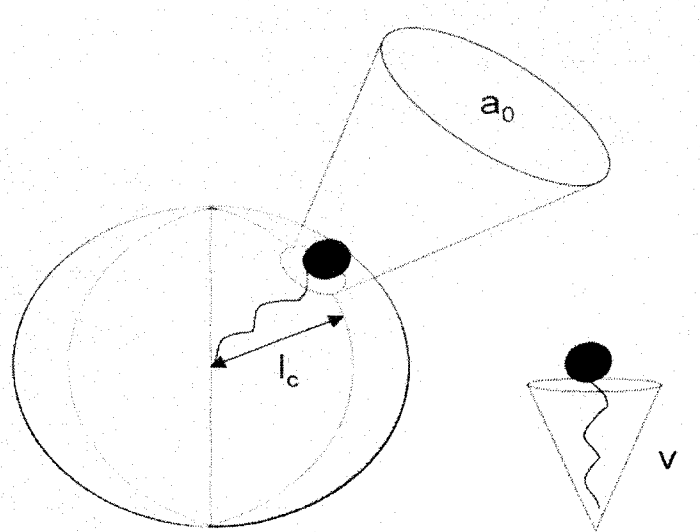
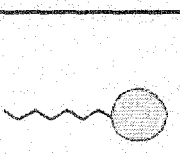
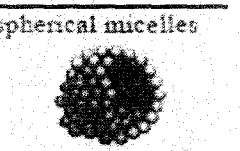
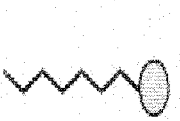
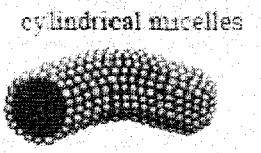
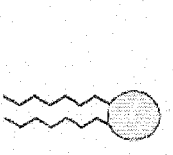
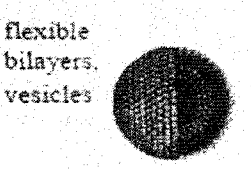
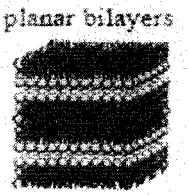
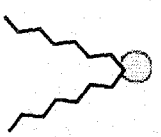
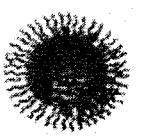


Figure 1.4: The critical packing parameter P (or surfactant number) relates the head group area, the extended length and the volume of the hydrophobic part of a surfactant molecule into a dimensionless number $P=V/a_0l_c$

The molecular packing parameter P is defined as the ratio $v/a_o l_c$, where v and l_c are the volume and the extended length of the surfactant tail, respectively and a_o is the *equilibrium* area per molecule at the aggregate interface (or mean cross-sectional {effective} head-group surface area), as illustrated in Figure 1.4. If we consider a spherical micelle with a core radius R, made up of N_{agg} molecules, then the volume of the core is $V = N_{agg} \times v = 4\pi R^3/3$, the surface area of the core $A = N_{agg} \times a_o = 4\pi R^2$. Hence, it can be deduced that $R = 3v / a_o$, from

Table1.1 Schematic representation of surfactant structures and shapes derived from various packing parameters

Possible surfactant type	P(=V/$a_o l_c$)	Shape	Structures formed
Single-tail surfactants with large head groups	p< 1/3		
Single chain surfactants with small head groups	1/3<P<1/2		
Double chain surfactants with large headgroups and flexible chains	1/2<P<1		
Double-chain surfactants with small head groups or rigid, immobile chains	P~1		
double-chain surfactants with small head groups, and bulky chain	P>1		

simple geometrical relations. If the micelle core is packed with surfactant tails without any empty space, then the radius R cannot exceed the extended length l_c of the tail. Introducing this constraint in the expression for R, one obtains $0 \leq v / a_o l_c \leq 1/3$, for spherical micelles. These geometrical relations, together with the constraint that at least one dimension of the aggregate (the radius of the sphere or the cylinder, or the half-bilayer thickness, all denoted by R) cannot exceed l_c, lead to the following well-known connection between the molecular packing parameter and the aggregate shape [7]. $0 \leq v / a_o l_c \leq 1/3$ for sphere, $1/3 \leq v / a_o l_c \leq 1/2$ for cylinder, and $1/2 \leq v / a_o l_c \leq 1$ for bilayer. Inverted structures are formed when $P>1$. Therefore, if the molecular packing parameter is known, the shape and size of the equilibrium aggregate can be readily identified as shown above. Noteworthy, a_o is often referred to as the "headgroup area" in the literature. This has led to the erroneous identification of a_o as a simple geometrical area based on the chemical structure of the headgroup in many papers, although a_o is actually an equilibrium parameter derived from thermodynamic considerations [6]. Needless to say, that for the same surfactant molecule, the area a_o can assume widely different values depending on the solution conditions such as temperature, salt concentration, additives present, etc.; hence, it is meaningless to associate one specific area with a given head group. For example, sodium dodecylbenzene sulfonate forms micelles in aqueous solution whereas bilayer structures are formed when alkali metal chlorides are added [10]. Moreover, the role of the surfactant tail has been virtually neglected. This is in part because the ratio v /l_c appearing in the molecular packing parameter is independent of the chain length for common surfactants (0.21 nm^2 for single tail surfactants) and the area a_o depends only on the head group interaction parameter. Nagarajan showed that the tail length influences the head group area (consideration of tail packing constraints) and thereby the micellar shape [6].

1.4 Self-Assembled Structures of Amphiphilic Molecules in Water

1.4.1 Micelles

The most intensely studied and debated type of molecular self-assembly and perhaps the simplest in terms of the structure of the aggregate is the micelle. Micelles formed by ionic amphiphilic molecules in aqueous solution are dynamic associations of surfactant molecules that achieve segregation of their hydrophobic portions from the solvent via self-assembly. They are loose, mostly spherical aggregates above their critical micellisation concentration

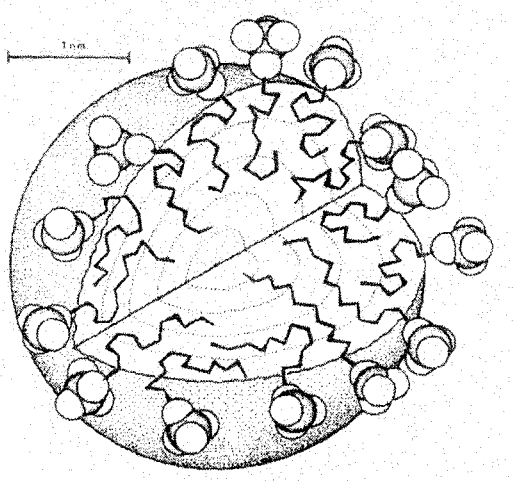


Figure 1.5: Schematic representation of a spherical micelle in aqueous solution.

(cmc) in water or organic solvents [1]. Also, micellar aggregates are short-lived dynamic species, which rapidly disassemble and reassemble [11]. Hence, only average shape and aggregation numbers of micelles can be determined. Micellization of surfactants is an example of the hydrophobic effect. In micellization there are two opposing forces at work. The first is the hydrophobicity of the hydrocarbon tail, favouring the formation of micelles and the second is the repulsion between the surfactant head groups. The mere fact that micelles are

formed from ionic surfactants is an indication of the fact that the hydrophobic driving force is large enough to overcome the electrostatic repulsion arising from the surfactant head groups. Figure 1.5 represents a spherical micelle formed in aqueous solution, where the hydrophobic chains are directed towards the interior of the aggregate and the polar head groups point towards water, hence allowing the solubility / stability of the aggregate (no phase separation). Micelles are also known to be disorganized assemblies whose interiors consist of mobile, non-stretched hydrophobic chains [12]. Note in addition that water molecules can penetrate partially into the micelle core to interact with surfactant hydrophobic tails [13]. There are a huge number of publications related to the micelles, micelle structures, and the thermodynamics of micelle formation. A huge amount of experimental and theoretical work devoted to the understanding of the aggregation of surface-active molecules has been carried out [14-16].

Micelles are generally formed by cationic, anionic, zwitterionic as well as nonionic surfactants having short alkyl chains. The environment of a micelle varies in a regular manner as a function of distance from the center of the micelle, going from a relatively dense aliphatic medium near the center to a relatively diffuse region known as either Stern layer in ionic micelles, or as Palisade layer in neutral micelles [17-19] where the head groups, bound counterions, and solvent molecules coexist. The remaining counterions are contained in the Gouy-Chapman portion of the double layer that extends further into the aqueous phase. Fluorescence probe studies have indicated that micellar core is nonpolar, but less fluid than hydrocarbon solvents of equivalent chain length [20]. On the other hand, the Stern layer has polarity equal to that of alcohols [21].

When a nonpolar group is introduced into an aqueous solution, the hydrogen bonding network formed by the existing water molecules is disrupted and the water molecules order themselves around the nonpolar entity to satisfy hydrogen bonds (Figure 1.6 A). This results in an unfavourable decrease in entropy in the bulk water phase. As additional nonpolar groups are added to the solution, they self-associate thus reducing the total water-accessible surface of the complex relative to the monodisperse state. (Figure 1.6 B) Now, fewer water molecules

are required to rearrange around the collection of nonpolar groups. Therefore, the entropy associated with the complex is less unfavorable than for the monodisperse detergents. In short, hydrophobic association and the formation of micelles is driven by the favorable thermodynamic effect on the bulk water phase.

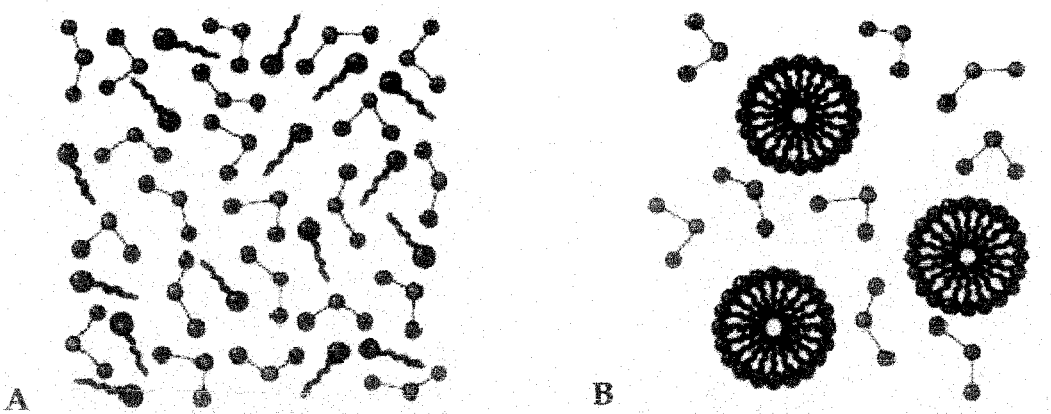


Figure 1.6: Water molecules ordered around surfactant monomers (**A**). Loss of total water-accessible surface as a result of micellisation (**B**).

A great deal of work has been done on elucidating the various factors that determine the cmc at which micelle formation becomes significant, especially in aqueous media. An extensive compilation of the cmcs of surfactants in aqueous media has been published [22]. Among the factors that are known to affect the cmc in aqueous solution are (i) the structure of the surfactant, (ii) the presence of added electrolyte (in the case of ionic surfactants) in the solution, (iii) the presence of various organic compounds in solution, and (iv) temperature of the solution.

Surfactant structure. In general, the ionic surfactants have higher cmc values compared to nonionic surfactants. The cmc in aqueous media decreases as the hydrophobic character of the surfactant increases. It has been observed that the cmc is halved by the addition of one methylene group to a straight-chain hydrocarbon tail. For nonionics and zwitterionics, the cmc value is decreased to one fifth of its previous value. The branching of the hydrocarbon chain appears to have about one-half the effect of carbon atoms of a straight chain. When C-C double bond is present in the hydrocarbon chain the cmc value is higher than that

of the corresponding saturated compound. An introduction of a polar group such as –O or –OH into the hydrophobic chain generally causes a significant increase in the cmc value in aqueous medium at room temperature. However, replacement of hydrocarbon chain by a fluorocarbon chain of same length causes a decrease in cmc value. For n-alkyl ionic surfactants, the cmc decreases in the order aminium salts > carboxylates > sulfonates > sulfates. It has been found that in quaternary cationics, pyridinium compounds have smaller cmcs than the corresponding trimethylammonium compounds.

Counterion. The degree of counterion binding, β (=1-α), has also an effect on the cmc value of ionic surfactants. The larger the hydrated radius of the counterion ($NH_4^+ > K^+ > Na^+ > Li^+$ and $I^- > Br^- > Cl^-$), the weaker the degree of binding, and hence larger the cmc. Thus in aqueous medium, for anionic lauryl sulfates, the cmc increases in the order $Ca^{2+} < N(C_2H_5)_4^+ < N(CH_3)_4^+ < NH_4^+ < Cs^+ < K^+ < Na^+ < Li^+$. On the other hand, for cationic dodecyltrimethylammonium and dodecylpyridinium salts, the order of decreasing in aqueous medium is $I^- < Br^- < Cl^- < F^-$.

Electrolyte. In aqueous solution, the presence of electrolyte causes a decrease in the cmc, the effect being more pronounced for anionic and cationic than for zwitterionic surfactants and more pronounced for zwitterionic than for nonionics. This is a consequence of decreased electrostatic repulsion between ionic headgroups in the micelle. The change in cmc of nonionics and zwitterionics upon addition of electrolyte is mainly due to the "salting out" or "salting in" of the hydrophobic group in aqueous solvent.

Organic additives. Water-soluble polar organic compounds such as alcohols and amides reduce the cmc at much lower concentrations. Shorter-chain alcohols are mainly adsorbed in the water-micelle interfacial region. The longer-chain compounds are adsorbed in the outer portion of the micelle core, between the surfactant molecules. Additives that have more than one group capable of

forming hydrogen bonds with water appear to produce greater depression of cmc. On the other hand, additives like urea, formamide, N-methylacetamide, guanidinium salts, short-chain alcohols, ethylene glycol, and other polyhydric alcohols, such as fructose and xylose increase cmc at relatively higher concentrations by modifying the interaction of water with surfactant molecules.

Temperature. The effect of temperature on the CMC of surfactants in aqueous medium is complex, the value appearing first to decrease with temperature to some minimum and then to increase with further increase in temperature. Increase of temperature causes decrease of hydration of the hydrophilic group, which favors micellization and also causes disruption of the structured water surrounding the hydrophobic group, which disfavors micellization. The relative magnitude of these two opposing effects, therefore, determines increase or decrease of CMC.

1.4.2 Worm-like micelles

Worm-like micelles are long, flexible, cylindrical chains with contour lengths of the order of a few micrometers. The entanglement of these wormlike chains into a transient network imparts viscoelatic properties to the solution [23-24]. Single chain ionic surfactants, e.g., cetyltrimethylammonium bromide (CTAB), favor convex-up surface geometry of the micelles due to strong headgroup repulsion and form spherical or near spherical micelles at the critical micelle concentration (cmc), while either at much higher surfactant concentrations (~1.0 M) or in the presence of high inorganic salt concentrations (>0.1 M), morphological changes occur to rod-like micelles and vesicles [27-30]. Hydrotropic salts like sodium salicylate (NaSal) also promote sphere to worm-like micellar transition at considerably lower concentration (e.g., ~1.0 mM in CTAB) by increasing the packing parameter above the critical value of 1/3 via efficient charge screening of the surfactant head groups [31]. These worm-like micellar solutions at low concentrations show complex and unusual rheological phenomena.

The dynamics of these systems differs from those of conventional polymers in that the wormlike micelles are continuously breaking apart and recombining. The rheological behavior of these surfactant solutions is known to follow "reaction-reptation model" which is an extension of the reptation model of polymer relaxation to cylindrical micelles of surfactant molecules undergoing reversible scission and recombination processes [25]. The linear and nonlinear viscoelastic properties of surfactant solutions have been extensively studied over past few years, both theoretically [26,27] and experimentally [28-38]. In general, it is observed that there is a critical shear rate above which the viscosity dramatically increases for dilute concentration of surfactant solution. The cause of this shear thickening phenomenon is believed to be the flow-induced structure of surfactant solution under shear flow [28,34].

Figure 1.7: Microstructure of a typical wormlike micelle.

With increasing flow intensity, the micelles undergo coalescence or tend to be stretched toward the flow direction, and as shear flow is going with time, the shear-induced structure of wormlike micelles continuously breaks down and re-forms at high shear rate [39]. This shear-induced structure (SIS) behaves like a gel and shows strong flow birefringence in solution state [31]. The classic example of such an 'abnormal' system is a solution containing cationic surfactant cetyl pyridinium chloride (CPC) with sodium salicylate (NaSal) as the additive. For

semidilute surfactant solutions, zero shear viscosity initially increased with concentration, reached a maximum, and then decreased [24,32,40]. Also, the shear viscosity of semi-dilute CPC/NaSal solutions showed almost a constant value until the critical shear rate and then shear thinning began, followed by shear thickening at higher shear rate.

The average micellar length is a thermodynamic quantity, and it responds to changes in solution composition and temperature. Normally when a wormlike micellar solution is heated, the micellar length decays exponentially with temperature [23,41]. The reduction in micellar length leads to an exponential decrease in viscosity of the solution. The reduction in micellar length, in turn, leads to an exponential decrease in rheological properties such as the zero-shear viscosity η_0 and the relaxation time t_R. Accordingly, an Arrhenius plot of ln η_0 versus 1/T (where T is the absolute temperature) falls on a straight line, the slope of which yields the flow activation energy E_a. Values of E_a ranging from 70 to 300 kJ/mol have been reported for various micellar solutions [41-43].

Inorganic and organic salts have been widely used as additives to facilitate the structural transition of micelles in ionic surfactant solutions [44-47]. Inorganic counterions promote gradual micellar growth by reducing the head group repulsions in the ionic micelles. On the other hand, organic salts in aqueous micellar systems, dissociate to produce ionic species with a hydrophobic moiety, which affects the packing of the surfactant tails and leads to changes in the effective packing parameter. The growth of cationic surfactant such as CTAB micelles has been extensively studied in the presence of salts such as KBr [48], sodium salicylate [49,50] chlorobenzoates [51], and benzyl sulfonates [52]. The increased salt concentrations cause the microstructure to change from globular to wormlike micelles. Addition of anionic surfactant, for instance, sodium dodecyl benzenesulfonate (SDBS) to solutions of cationic surfactants has also been found to generate wormlike micelles [53]. Kaler and coworkers have reported a million-fold increase in viscosity for mixtures of alkyltrimethylammonium bromide surfactants and sodium oleate (SO) relative to the single component solution [54]. The effect of nonionic additives on micellar shape has also been investigated by

many research groups. Hedin and co-workers have reported the elongation of CTAB micelles upon the solubilization of benzene [55]. Zhang and coworkers investigated the effect of benzyl alcohol on CTAB/KBr micellar systems through a combination of rheology and NMR and have suggested elongation of micelles upon alcohol solubilization [56]. The addition of alcohols has also been shown to promote growth of worm-like micelles in such transitions [57-59].

Although, studies related to the microstructural transitions of micelles to worm-like micelles and vesicles have been going on for quite some time, a common element in most of the works summarised above is the presence of an anion salt like NaSal. A number of studies on micellar shape transition in cationic, anionic, and catanionic surfactant systems induced by polar and nonpolar organic species have been reported the literature [55, 60-62]. However, these systems trigger the shape transition only at very high concentrations and make themselves unsuitable for certain applications. Recent studies show that the above mentioned transitions takes place even in presence of neutral aromatichydroxy dopants like 1- and 2-naphthols. Studies on the microstructural modifications by neutral aromatichydroxy compounds are rather recent and will be discussed later in more detail.

1.4.3 Vesicles

Vesicles are closed bilayered structures similar to those of the lamellar phase characterized by two distinct water compartments, one forming the core and other the external medium [63,64]. Like micelles, the formation of vesicles is a result of energetically favorable hydrophobic association of the hydrocarbon tail(s) of an amphiphilic molecule. However, unlike micelles vesicles have two distinct domains: the lipophilic membrane and the interior aqueous cavity.

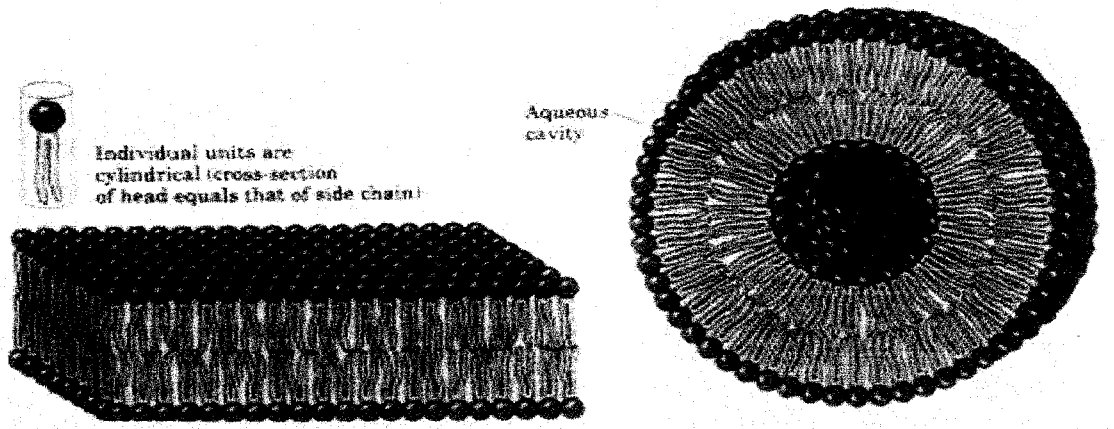


Figure 1.8: Figure showing bilayer and the individual unit of the surfactant forming the bilayer. The folding of the bilayer due to hydrophobic interaction forms the vesicle.

Specifically, the surface of micelles is a lipid monolayer, while the surface of liposomes is a lipid bilayer and the inner core of micelles is composed of hydrocarbon chains, while the inner core of vesicles is an aqueous phase. Vesicles have been found useful as agent in many practical applications and also a basis for several theoretical investigations. Micelles can solubilize amphiphiles and organic compounds, while vesicles can solubilize (or encapsulate) organic compounds and amphiphiles found in the lipid bilayer, and inorganic compounds and amphiphiles found in the aqueous core.

Vesicles can be prepared as small unilammellar vesicles (SUV), large unilamellar vesicles (LUV) or large multilamellar vesicles (liposomes). Multilamellar vesicles can be large having diameter of several μms and they are also termed as onions [65,66]. Vesicles are classified in terms of number of lamellae and size. Figure 1.7 presents a schematic view of the major liposome types. Multimembrane vesicles are divided into three groups: multilamellar vesicles (MLVs) also called as onion-shaped vesicles, oligolamellar vesicles (OLVs), and multivesicular vesicles (MVVs). OLVs are composed of several lamellae.

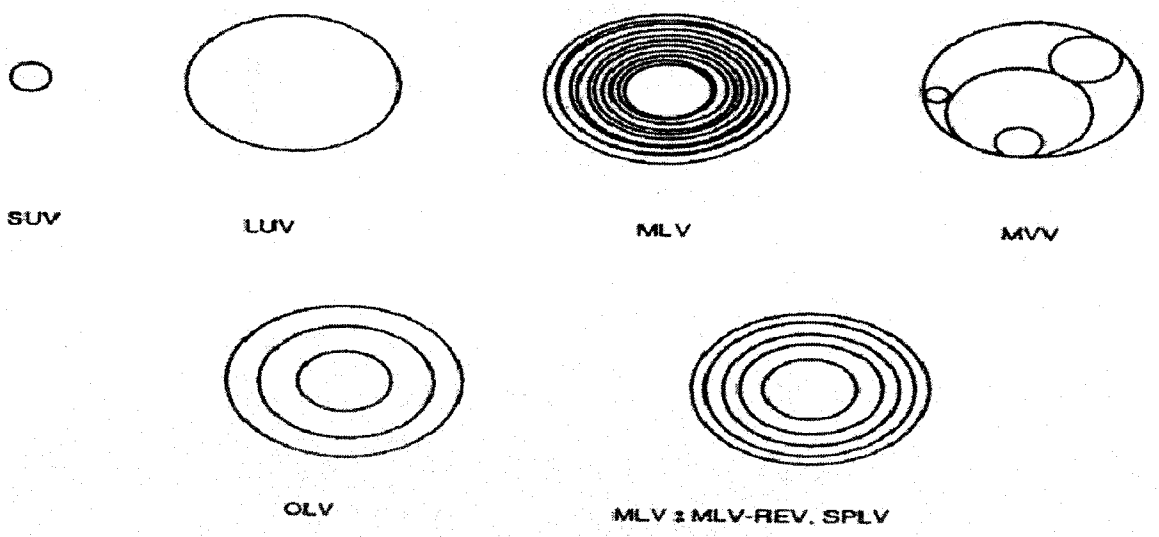


Figure 1.9: Morphology of different vesicle structures

Unilamellar vesicles consist of a lipid bilayer separating an aqueous solution from the bulk phase, forming roughly spherical structures with an inner aqueous core [67,68]. These vesicles (ULVs) are usually divided into three groups in terms of size: small unilamellar vesicles (SUVs), large unilamellar vesicles (LUVs), and giant unilamellar vesicles (GUVs). Vesicles under 100 nm are normally considered as SUVs, whereas those greater than 100 nm are LUVs. GUVs are those, which have sizes greater than 10 μm. The disadvantage of MLVs is their heterogeneous size distribution. The advantage of SUVs is the homogeneous size distribution and their disadvantage is low encapsulation efficiency. For LUVs, encapsulation efficiency is relatively high and macromolecules can be encapsulated. Vesicles have been found to form from synthetic surfactants containing one, two, or three alkyl hydrocarbon chains and quaternary ammonium, carboxylate, sulfate, sulfonate, hydroxide, or phosphate, zwitterionic or functionalized head groups. Vesicles are also generated by polymeric surfactants and block copolymers.

Role of Hydrogen Bonding Interaction in Self-Assembly Formation

Hydrogen bonds play very important role in biological systems. Hydrogen bonds have directional property and are moderately strong (4-25 kJ mol^{-1}) [69,70]. One of the important features of hydrogen bonding is that the bond formation can be reversibly switched under mild conditions by physical stimuli such as heat. In fact, hydrogen bonds have become a tool in liquid crystal (LC) [71,72] and polymer [73,74] chemistry. The role of hydrogen bonding on the gelation of organic solvents and water is well documented in the literature [74,75]. Recent studies have shown that short range attractive interactions, such as hydrogen bonding could be a driving force in the formation of bilayer self-assemblies of single-chain surfactants [76,77, 78-80]. In fact, hydrogen bonding between the amide groups is responsible for the favorable aggregation of some cationic surfactants that carry amidegroup spacer between the hydrophobic tail and the quaternary ammonium ion [81-84]. It has also been shown that intermolecular hydrogen bonding (IHB) between secondary amide groups in the hydrophobic tail of sodium 11-acrylamidoundecanoate induces a stable linear state [48].

It is well known that the spontaneous curvature of a surfactant aggregate is related to the relative sizes of the hydrophilic head and hydrophobic tail of the surfactant molecule. Increase of attractive forces between the headgroups can cause a decrease in effective head-group area, and hence a decrease in the curvature of the aggregate. In other words, this is a driving force for aggregate growth. LBM studies at the air-water interface have suggested that OH-substitution near (2 or 3-position) the headgroup results in a loss of ordering which is caused by the headgroup enlargement by the neighboring –OH group and a misfit of the alkyl chains in hydroxypalmitic acid [85]. On the other hand, well-shaped condensed phase domains were found after the phase transition in 9-hydroxypalmitic acid in which the -OH group is near the center of the hydrocarbon chain. The stability of the LC phase formed by the fatty acid derivatives bearing the -OH group is influenced by the ability of the substituent to form IHB and cause little disorder in the packing of the alkyl chain. The hydrogen-

bonding role of -OH group in molecular cohesion in condensed monolayer, helical ribbon, and gel formation by 12-hydroxyoctadecanoic acid has been reported by Tachibana and coworkers [86,87].

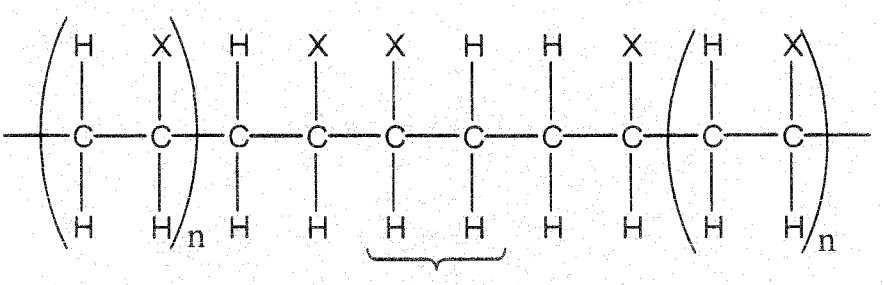
1.5 Biodegradable Polymers:Poly(vinylalcohol) and Sodium alginate.

Increasing concern exists today about the preservation of our ecological systems. Most of today's synthetic polymers are produced from petrochemicals and are not biodegradable. Persistent polymers generate significant sources of environmental pollution, harming wildlife when they are dispersed in nature. For example, the disposal of non-degradable plastic bags adversely affects sea-life. It is widely accepted that the use of long-lasting polymers in products with a short life-span, such as engineering applications, packaging, catering, surgery, and hygiene, is not adequate. Moreover, incineration of plastic waste presents environmental issues as well since it yields toxic emissions (e.g., dioxin). Synthetic plastics are resistant to degradation, and consequently their disposal is fuelling an international drive for the development of biodegradable polymers. Biodegradable polymers have been a subject of interest for many years because of their potential to protect the environment by reducing non-biodegradable synthetic plastic waste [88–92]. Biodegradation involves enzymatic and chemical degradation by living microorganisms [93–95].In essence, the enzymatic degradation of polymers takes place by hydrolysis and oxidation.The Biodegradable polymers, i.e.biopolymers are polymers formed in nature during the growth cycles of all organisms; hence, they are also referred to as natural polymers. Their synthesis generally involves enzyme-catalyzed, chain growth polymerization reactions of activated monomers, which are typically formed within cells by complex metabolic processes.

The applications of biodegradable polymers have been focused on three major areas:medical, agricultural, and consumer goods packaging. Some of these have

resulted in commercial products. Because of their specialized nature and greater unit value, medical device applications have developed faster than the other two.

1.5.1 Poly (vinyl alcohol) :



where X is- OH

Figure 1.10: A general structure of poly vinyl alcohol

(Poly vinyl alcohol)(PVA) is the most readily biodegradable of vinyl polymers. It is readily degraded in waste-water-activated sludges. The microbial degradation of PVA has been studied, including its enzymatic degradation by secondary alcohol peroxidases isolated from soil bacteria of the Pseudomonas strain [96–99]. It was concluded that the initial biodegradation step involves the enzymatic oxidation of the secondary alcohol groups in PVA to ketone groups. Hydrolysis of the ketone groups results in chain cleavage. Other bacterial strains, such as Flavobacterium [99] and Acinetiobacter [100] were also effective in degrading PVA. The controlled chemical oxidation of PVA was carried out to yield poly(enol-ketone) (PEK), which has a similar structure to the intermediate formed as PVA is biodegraded [101].Poly (vinyl alcohol) (PVA) has attracted much attention in recent years due to its excellent flexibility, transparency,toughness, and relatively low cost, especially in the era of highprice petroleum. PVA has been widely used in different fields such as textile sizing and has been utilized as a finishing agent, an emulsifier, a photosensitive coating, and as an adhesive for paper, wood,

textiles, and leather [102,103]. In addition, it is a biologically friendly polymer because of its biodegradability and biocompatibility[104].

Poly (vinyl alcohol) is an industrially important polymer, and this is shown by the fact that its production increases every year [105-109]. It exhibits a high degree of compatibility with inorganic salt solutions[110] natural and synthetic resins, and other chemicals [111,112]. Small amounts effectively stabilize emulsions [113] dispersions, and suspensions[114] It also forms chemical complexes of practical importance [115]. The intrinsic viscosity [η], a measure of the size of the isolated molecules,and Huggin's constant K_H [116],a measure of their interactions with solvent, are both influenced by changes of solvent power [117] and temperature [118] .Besides theoretical interest,such measurements are also important for technical reasons including polymer addition in motor oil recovery. Advances in the preparation of stereoregular polymers have stimulated the need to characterize their microtacticity and fine structure [119]. A number of studies and experimental techniques were used to characterize the nature of polymers in different solvents, but there seems to be few systematic studies of the dilute solution properties in different solvents and that too restricted to one or two temperatures[120,121]. As far as the polymers are concerned, the viscosity method can be successfully employed for the determination of the nature of the compound and their behavior in different solvents. Viscosity is affected by a number of parameters such as molecular mass, shape, and size of molecules, concentration, temperature, and intermolecular attractions, viz., ion-ion and ion-solvent interactions [110,122] .Ahmed et al.Takada et al., and Wang et al.[123-125] studied the thermodynamics of supermolecular order of the polymer PVA in aqueous solutions by the viscometric behavior and light scattering studies [124,125]

1.5.2 Sodium Alginate

Sodium alginate is a family of linear, binary co-polymers of (1→4) linked β-D-mannuronate (M) and α-L- guluronate residues arranged in a non-regular,

blockwise fashion along the chain [126,127]. The chain is composed of homopolymeric blocks of mannuronate (MM) and guluronate (GG),and blocks with an alternating sequence (Fig-1.11) The chain conformations of M- block and G- block were suggested to be "flat-ribbon" and "buckled-ribbon" forms,respectively [128].From light scattering and viscometric data, Smidsrod showed that the relative extension in the unperturbed state of the three types of blocks increase in the order of MG block ‹ MM block ‹ GG block [129]. Thus alginate polymer with high content of guluronate and long G-blocks generally showed a more extended, less flexible chain conformation than long M-block alginates. In general, the relative dimensions for the neutral unperturbed alginate chain at theta condition, a measure of chain stiffness, was higher than that of carboxyl methyl cellulose, dextran and amylase, but lower than double stranded DNA [130]

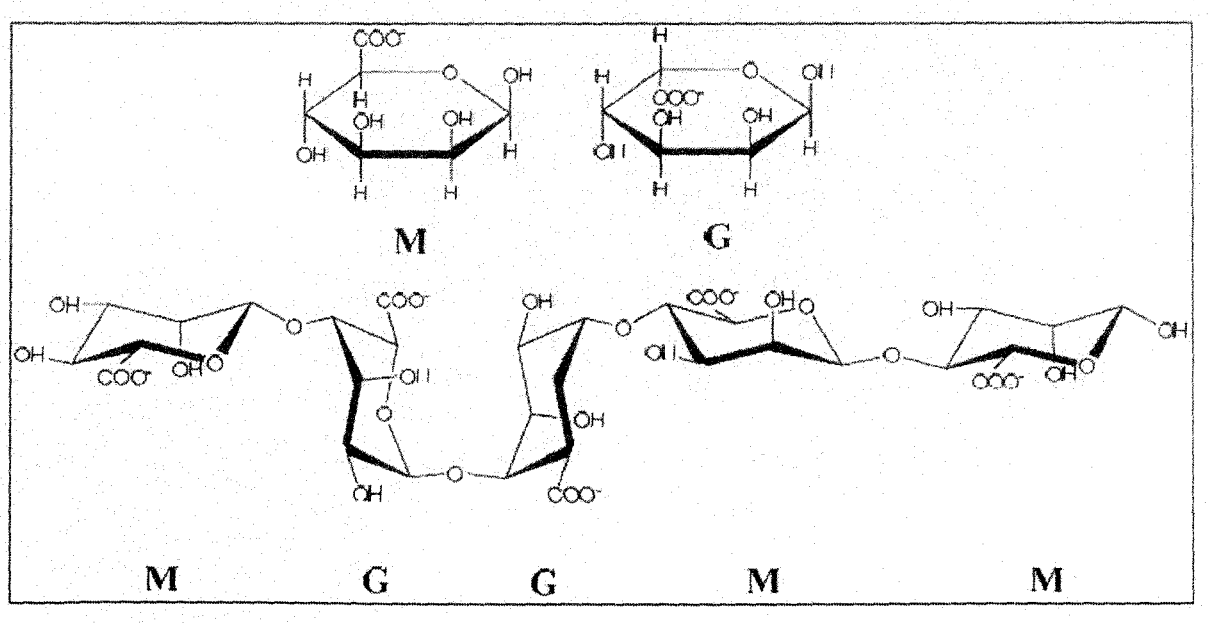


Figure 1.11: The chemical structure of alginate; the top figure illustrates the two monomers: mannuronic acid (M) and gluronic acid (G) residues in their Haworth conformation where as the bottom figure shows a sample block structure of alginate.

The biological properties of polysaccharides, especially of the algínates, have been explored since many decades in countless medical and surgical

applications. Those properties, and the solubility in water, are due to the presence of inorganic ions in the alginate structure[131]. Alginic acid form water-soluble salts with monovalent cations but is precipitated upon acidification. Alginates of many bivalent cations, particularly of $Ca^{2+,}$ Sr^{2+} and $Ba^{2+,}$ are insoluble in water and can be prepared when sodium ions of NaAlg are sodium alginate has been employed in the preparation of gels for the delivery of biomolecules such as drugs, peptides and proteins [136].Toxicological data replaced by di- and trivalent cations This property is used in the isolation of alginic acid from algae [132,133]. Due to their physical and chemical properties alginic acid (HAlg)and sodium alginate (NaAlg), have widely been used in food processing, medical and pharmaceutical industries [134] such as drug carrier [135], moreover, showed that alginates are safe when used in food. HAlg and its derivatives acts as stabilizers and thickeners facilitating the dissolution and improving viscosity of the ingredients preventing the formation of crystals that will prejudice the appearance and homogeneity, mainly in frozen products [137].

Alginates are fainly characterized of the marinepolysaccharides [138].Most commercial alginates are extracted from brown seaweed. However alginates can also be synthesized by some bacterial species such as Azotobacter and Pseudomonas[138]. Bacterialalginates are additionally O-acetylated on the 2 and/or 3 positions of the D-mannuronic acid residues, and exhibit a greater water binding ability [139,140]. Among the brown algal species, the most widely used are Laminaria hyperborea, Macrocystis pyrifera, and Ascophyllum nodosum due to their abundance [141] for extracting alginates.

1.6 Reference

1. J.H. Fuhrop and J. Köning, In *Membranes and Molecular Assemblies: the `Synkinetic `Approach*, The Royal Society of Chemistry - Cambridge, (1994).
2. J.H.Clint, *Surfactant Aggregation*, Blackie - Glasgow/London, (1992).
3. J.H.Fhurhop and J.Mathieu, *J. Chem Soc., Chem. Commun* , 144 (1983).
4. M.J.Rosen,*Surfactants and Interfacial Phenomena*, Wiley-Interscience,p.60. (2004).
5. E.Kissa, In *Fluorinated Surfactants and Repellents*, 2nd ed.; Marcel Dekker:`New York; p103 (2001).
6. R. Nagarajan *Langmuir*, **18**, 31 (2002)
7. J.N.Israelachvili ; D.J. Mitchel, and B.W. Ninham, *J. Chem. Soc., FaradayTrans.* **72(2)**, 1525 (1976).
8. J.N. Israelachvili In *Intermolecular and Surface Forces*; Academic Press: London, (1994).
9. R.Nagarajan; Ruckenstein, E. In *Equations of State for Fluids and Fluid Mixtures*; `J.V.Sengers, R.F.Kayser, C.J. Peters, Jr.White and H.J. Eds.; *Elsevier*: Amsterdam, `Chapter 15 (2000).
10. A. Sein and J. B. F. N. Engberts, *Langmuir,* **11**, 455 (1995).
11. A.Patist, S.G.Oh, R.Leung and D.O.Shah, *Coll. Surf. A*, **176**, 3 (2001)
12. F.M. Menger, R Zana and B.Lindman, *J. Chem. Ed.* **75**, 115 (1998).
13. K.Tsujii, In *Surface Activity: Principles, Phenomena, and Applications*; Academic Press Ed.: San Diego, London, New York, Tokyo, (1997).
14. R.G.Laughlin, *The aqueous phase behavior of surfactants*; Academic Press: `London,(1994).
15. J. H. Fendler *Membrane Mimetic Chemistry*, Wiley: New York, (1982).
16. J.H. Fuhrhop and W. Helfrich, *Chem. Rev.*, **93**, 1565 (1993).
17. S.S.Berr, E.Caponetti, J. S.Johnson, R.R.M. Jones and L. Majid, *J. Phys. `Chem*, **90,** 5766 (1986).

18. S. S. Berr , M.J. Coleman, R. R.M. Jones and J. S. Johnson, *J. Phys. Chem.*, **90**, 6492 (1986).

19. S. S. Berr ,*J. Phys. Chem.*, **91**, 4760 (1987).

20. N. J.Turro, M.Gvätzel and A. M. Brann, *Angew. Chem. Int. Ed.*, **19**, 675 (1980).

21. R. Zana, In *Surfactant Solutions. New Methods of Investigation*, R. Zana, and`M.Dekker New York, Chapter 5 (1987).

22. P.Mukherjee and K. J. Mysels, *Critical Micelle Concentrations of Aqueous Surfactan Systems*, NSRDS-NBS 36, U. S. Dept. of Commerce, Washington, DC, (1971).

23. M. E. Cates and S. J. Candau, *J. Phys.: Condens. Matter*, **2**, 6869 (1990).

24. H. Hoffmann In *Structure and Flow in Surfactant Solutions*; C. A. Herb and R.K.Prudhomme, Eds.; American Chemical Society: Washington, DC, ***2,3*** pp 2-31(1994).

25. M.E.Cates, *Macromolecules* **20**, 2289 (1987).

26. M.E.,Cates, In Theoretical modeling of viscoelastic phases, C.A. Herb, and R.K. Prudhomme (eds), *ACS Symposium Series* **578**, 32 (1994).

27. M.E.Cates, and S.J.Candau,Statics and dynamics of worm-like surfactant micelles, *J. Phys.* **2**, 6869 (1990).

28. H. Hu, R.G. Larson and J.J. Magda, *J. Rheol.* ***46***, 1001 (2002).

29. T.Shikata, M. Shiokawa, S. Itatani and S. Imai, *Korea Australia Rheol. J.* `***14***,129 (2002).

30. Z. Lin, A. Mateo, E. Kesselman, E. Pancallo, D.J. Hart, Y. Talmon, T.H.Davis, L.E. Scriven and J. Zakin, *Rheol. Acta* **41**, 483 (2002).

31. Z.Lin, B. Lu, J. Zakin, Y. Talmon, Y. Zheng, T.H. Davis and L.E. Scriven, *J. Colloid Interface Sci.* ***239***, 543 (2001).

32. H. Rehage and H. Hoffmann *Mol. Phys.*,**74**, 933 (1991).

33. H.Hoffmann, H. Löbl, H. Rehage and I.Wunderlich *Tenside Detergents,* **22**,290 (1985)

34. H. Rehage and H. Hoffmann *Phys. Chem.*,**92**, 4712 (1988).

35. T.Shikata, K.Hirata and T.Kotaka *Langmuir.*,**3**, 1081 (1987)

36. T.Shikata., K. Hirata and T. Kotaka, *Langmuir,* **4**, 354 (1988)

37. T.Shikata., K. Hirata and T. Kotaka, *Langmuir*, **5,** 398 (1989)

38. T.Shikata., K. Hirata and T. Kotaka, *J. Phys. Chem,* **94**, 3702 (1990)

39. W.J. Kim and S.M. Yang, *Langmuir* **16**, 4761 (2002).

40. R.Zana, *Adv. Colloid Interface Sci.* **97**, 205 (2002).

41. S. R., Raghavan and E. W. Kaler, *Langmuir*, **17**, 300 (2001)

42. R. Makhloufi and R.Cressely, *Colloid Polym. Sci.* **270**, 1035 (1992).

43. A., Ponton, C., Schott and D. Quemada, *Colloids Surf. A.*, **37**,145 (1998).

44. O. R.Pal, V. G. Gaikar, J. V. Joshi, P. S.Goyal and V. K. Aswal, *Langmuir*, **18**, 6764(2002).

45. G. Porte and J.Appell, *J. Phys. Chem,* ***85***, 2511 (1981).

46. E. W. Kalu, K. L. Herrington, D. J. Iampietro, B. Coldren, H. T. Jung, A. J. Zasadzinski, In *Mixed Surfactant Systems* 2nd Ed.; M. Abe, J.Scamehorn, Eds.; Marceel Dekker: New York (2005).

47. D.Angeleseu, A. Khan and H. Caldaram, *Langmuir*, **19**, 9155 (2003).

48. V. K.Aswal and P. S. Goyal, *Chem. Phy. Lett.*, **357**, 491 (2002).

49. H. Hoffmann, H. Rehage, G.Platz, W. Schorr, H.Thurn and W. Ulbricht, *Colloid Polym. Sci*, **260**, 1042 (1982).

50. P. A.Hassan and J. V. Yakhmi, *Langmuir*, **16**, 7187 (2000).

51. U.R.K. Rao, C. Manohar, B. S. Valaulikar, R. M. Iyer, *J. Phys. Chem.*, **91,** 3286 (1987).

52. O. R. Pal, V.G. Gaikar, J. V. Joshi, P. S. Goyal and V. K. Aswal, *Langmuir*, **18**,6764 (2002).

53. E.W.Kalu,K.L.Herrington D.J.lampietro,B.Coldren,H.T.Jung, A.J. Zasadzinskiln *Mixed Surfactant Systems* 2nd Ed.; M. Abe, J.Scamehorn, Eds.; Marceel Dekker: NewYork (2005).

54. D. Angeleseu, A. Khan and H. Caldaram, *Langmuir*, **19**, 9155 (2003).

55. N.Hedin, R.Sitnikov, I.Furo, U.Henriksson and O.Regev, *J.Phys.Chem.B* ,**103**, 9631 (1999).

56. W.C.Zhang, G.Z. Li, Q. Shen and J.H. Mu, *Colloids Surf., A, **170**,* 59 (2000).

57. S.Chiruvolu, H. E. Warriner, E.Naranjo, S.H.J.Idziak, J.O.Rädler, R.J.Plano, J.A .Zasadzinski and C. R. Safinya, *Science*, **266**, 1222 (1994).

58. (a) H. Hoffmann, C.Thunig and M. Valiente, *Colloids Surf* ,**67**, 223 (1992). (b) H.Hoffmann, U. Munkert, C.Thunig and M. Valiente *J. Colloid Interface `Sci.*, **163**, 217(1994). (c)M.Gradzielski, M. Bergmeier, M. Müller, H. Hoffmann, *J. `Phys.Chem B*, **101**, 1719 (1997).

59. R. Oda, L. Bourdieu, M. Schmutz, *J. Phys. Chem. B*, **101**, 5913 (1997)

60. C.Manohar, In *Micelles, Microemulsions, and Monolayers*; *Science and Technology*;D. O. Shah, Ed.; Marcel Dekker, Inc.: New York, p 145 `(1998).

61. P. M. Lindemuth and G. L. Bertrand, *J. Phys. Chem,* **97**, 7769 (1993).

62. H.Yin, S.Lei, S.Zhu, J.Huang and J.Ye, *Chem.-Eur. J*, **12**, 2825 (2006).

63. D.B. Fenske, N. Maurer and P. R. Cullis, In *Liposomes: a practical approach*, 2nd ed.; V.Weissig, Ed.; Oxford University Press: Oxford, p 167-191 (2003).

64. K. M. G. Taylor and S. J. Farr In *Liposomes in drug delivery*; H. M. Patel, Ed.; Harwood Academic Publishers: Chur, Switzerland, **2**, 95 (1993).

65. H. Hoffmann, and W. Ulbricht, *Recent Res. Devel. in Physical Chem.*, 2 (1998).

66. Susanne Nilsson, Krister Thuresson, Per Hansson and Björn Lindman, *J Phys.*

Chem. B, 102,7099 (1998).

68. D.D. Lasic, *Liposomes. From Physics to Applications*, Elsevier, Amsterdam,(1993).

69. I.I. Yaacob and A. Bose, *J. Colloid Interface Sci*, ***178,*** 638 (1996).

70. R.D. Koehler, S. R. Raghavan and E. W. Kaler, *J. Phys. Chem.`B*,**104**,11035(2000).

71. L. L. Brasher, K. L. Herrington, E. W. Kaler ,*Langmuir*, **11**, 4267(1995).

72. M. T. Yatcilla, K. L. Herrington, L. L. Brasher, E. W. Kale , S.Chiruvolu and J. A. Zasadzinski . *J. Phys. Chem*, **100**, 5874 (1996).

73. A. J. O'Connor, T. A. Hatton and A. Bose, *Langmuir*, **13,** 6931(1997).

75. N.Filipović-Vinceković, M. Bujan, , I. Šmit Lj.Tušek-Božić, and I. Štefanić, *J. Colloid Interface Sci.*, **201**, 59 (1998).

77. Y. Talmon, D. F.Evans and B. W. Ninham, *Science*, **221**, 1047 (1983).

78. K. K. Karukstis, S. W. Suljak, P. J. Waller, J. A.Whiles and E. H. Z. Thompson, *J. Phys.Chem*, **100**, 11125(1996).

80. E.F. Marques, A.Khan, M. da Graca Miquel and B. Lindman *J. Phys. Chem.*, **97**, 4729 (1993).

81. E.F. Marques, A.Khan and B. Lindman, *Thermochim Acta*, **394**, 31(2002).

82. G. Bai, Y. Wang, J. Wang, B. Han and H. Yan, *Langmuir*, **17**, 3522 (2001).

83. A.Das Burman, T. Dey, B.Mukherjee and A. R. Das, *Langmuir*, **16**, 10020 `(2000).

84. A. Bumajdad, J. Eastoe, P. Griffiths, D. C. Steytler, R. K. Heenan and J. R Lu, *et al. Langmuir*, **15**, 5271 (1999).

85. Y.Kondo, H. Uchiyama, N. Yoshino, K.Nishiyama and M. Abe, *Langmuir*, **11,**`2380 (1995).

86. E. F.Marques, O.Regev, A. Khan, M. da Graca Miquel, and B. Lindman, *J. Phys. Chem. B*, **103**, 8353 (1999).

87. D.J Iampietro,.L.L.Brasher, E.W. Kaler,A. Stradner and O. Glatter, *J.Phys. Chem B*, ***102***, 3105 (1998).

88. Y.Doi and K .Fukuda, editors. In *Biodegradable plastics and polymers* : *Elsevier* Amsterdam, (1994).

89. W.M. Doane, C.L.Swanson and Fanta GF. *Emerging technologyes for materials and chemicals from biomass*. ACS Symposium Series;**476**:,197 (1992).

90. D .Raghavan. *Polym-Plast Technol Eng*; **34**,41 (1995)

91. J.M. Krokhta, D. Mulder and C.L.C Johnston. In: *Biodegradable polymers `from agricultural products*. ACS Symposium Series ,**647**,120 (1996).

92. A.M. Thayer, *Plastics recycling efforts spurred by concerns about soli waste*. In:J.E, Glass, and G Swift, editors. *Agricultural and synthetic `polymers `Biodegradability and utilization*. ACS Symposium Series;**433**,38 (1990).

93. P.A. Wagner, B.J. Little, K.R Hart and R.I Ray *Int Biodeterior Biodegrad*,**38**,125 (1996).

94. L. Tilstra, D. J .Johnsonbourgh, *Environ Polym Degrad* **1**,247 (1993).

95. M. Vert, L.Feijen, A. Albertsson and G. Scott, editors. *Biodegradable polymers and plastics*.Wiltshire, UK: Redwood Poss Ltd, The Royal Society of Chemistry (1992).

96. T. Suzuki, *J. Appl. Polym. Sci. Appl. Polym. Symp.*, **35,** 431(1979).

97. Y.Watanabe, M.Morita, N. Hamade, and Y. Tsujisake, *Agric. Biol. Chem.*, **39,** 2447(1975).

98. M. Morita, and Y.Watanabe, *Agric. Biol. Chem.*, **41,** 1535 (1977) .

99. Y.Watanabe, N. Hamada,., M. Morita, and J.Tsuisake, *Arch. Biochem. `Biophys.*, **174,**575 (1976)

100. F.Fukanage, S.Sumina,K.Neda, T.Takemasa, and K.Tachibana, *Jpn. kokai*,**794**,471(1977).

101. F.Fukunaga, K. Nesta, K.Tuchibana, T. T Akemara, and S. Sumina, *Jpn. kokai*,**25**,786 (1976).

102. C. A. Finch, *Poly Vinyl Alcohol*; Wiley: New York, pp 1-3 and12-18 (1992).

103. N.Nakano, S.Yamane and K.Toyosima, *PoVal(polyVinyl-alcohol)*; Japan Polymer Society: Kyoto, p 3 (1989).

104. E.Chiellini, A.Corti, S. D Antone and R. Solaro, Biodegradation of poly (vinyl `alcohol) based materials. *Prog. Polym. Sci.*, **28**, 963 (2003).

105. N.Gungor and S. Dilmac, The effects of some salts and (NaPO3)*n* `polymer on viscosity of Na-Montmoillanite slurry. *J. Chem. Soc.Pak.*, **19**,14 (1997).

106. F.Uddin, V.Saeed and R. Talib, Temperature Dependence of the Intermolecular Activation Energy for Flow in Strontium Nitrate And Barium Nitrate Solution in Aqueous 2-Propanol Mixtures. *J. Saudi Chem. Soc.*, **2**, 101(1998).

107. R.H Stokes and R.Mills, *Viscosity Electrolyte and Related `Properties*;Pergamon Press: New York, 1965.

108. N. Ahmed, SAkber, I.Khan, and A. Saeed, Viscosity Parameters and `Energy of Activation of Dilute Aqueous Polyvinyl Alcohol (PVOH) `Solutions. *J. Chem. Soc Pa* **10**, 43(1998).

109. M. S.Khan and F. Kanwal, Degradation of PVC in Air. *J. Chem. Soc. Pak.*, **19**, 8 (1997).

110. H.Yang, P. Zhu, C. Peng, S. Ma, Q. Zhu and C. Fan, Viscometric Study of Polyviny Alcohol in NaCl/Water Solutions ranged from Dilute to Extremely Dilute Concentration.*Eur. Polym. J.* **9**, 1939 (2001)

111. N.M. Claramma, and N. M. Mathew, Rheological Behavior of Prevuleanized

Natural Rubber Latex; Huething Gm B H: Heidelberg, Germany, (1998).

112. T. Okaya, H. Kohna, K.Terada, T.Sato, H.Maruyams and J. Yamauchi,. Specific Interaction of Starch and Polyvinyl Alcohols having Long Alkyl Groups. *J. Appl.Polym. Sci.* **45**, 1127(1992).

113. M. Nakamae, K. Yuki, T.Sato and H. Maruyama, *Colloids and Surfaces, A, Physicochemical and Engineering Aspects*; Elsevier Science Publishers B. V Amsterdam, The Netherlands, (1997).

114 W. S. Lyoo, S. M. Lee, K. Koo, J. S. Lee, H. D. Ghim, J. P. Kim and J. Lee,Effect of Emulsion Polymerization Conditions of Vinyl Acetate on Viscosity Fluctuation and Gelatinous Behavior of Aqueous Poly (Vinyl`Alcohol) Solution. *J. Appl. Polym. Sci.* **82**, 1897(2001)

115. M.Shibayama, F. Ikkai, R. Moriwaki, and S. Nomura, Complexation of Poly (Vinyl Alcohol) - Congo Red Aqueous Solutions. 1*Viscosity Behav. Gelatin Mech. Macromol* , ***27***, 1738 (1994).

116. K.Lewandowska,D.UStaszewska,andM.Bohdanecky,Huggins Viscosity Coefficient of Aqueous Solutions of Poly (Vinyl Alcohol). *Eur. `Polym. J.*, **37**, 25(2001).

117. G. O Yahya,.; A. Ali, M. Al-Naafa and A. E. Z. Hammad, *J. Appl. Polym. Sci.*`**57**,343(1995).

118. K.Koga, A.Takada and N. Nemoto, Dynamic Light Scattering and Dynamic Viscoelasticity of Poly (Vinyl Alcohol) in Aqueous Borax Solutions. 5. Temperatures Effects. *Macromolecules*, ***32***, 8872(1999).

119. N.Ahmed,.and B. Ahmed, Intrinsic Viscosity, Huggins Constant and Unperturbed Chain Dimension of Poly Vinyl Pyrolidone. *J. Chem. Soc. Pak.*, **12**, 246(1990).

120. S.Shaikh, S. K. A Ali ;A. E. Z. Hamad, M.Al-Nafaa, A. Al- Jarallah and B. Abu-Sharukh, Synthesis,Characterization and Solution Properties of Hydrophobically Modified Poly (Vinyl Alcohol). *J. Appl. Polym. Sci.*, **70**, 2499 (1998).

121. M.Liu,R.Cheng,C.Wu and R.Qian, Viscometric Investigation of `Intramolecular Hydrogen Bonding Cohesional Entanglement in Extremely Dilute Aqueous Solutions of Polly Vinyl Alcohol. *J. Polym. Sci., Part B: Polym. Phys.*, **35**, 2421(1997).

122. G.Jones, and M. Dole, The Viscosity of Aqueous Solutions of Strong Electrolytes with Special Reference of Barium Chloride. *J. Am. Chem. Soc. (*1929).

123. N. Ahmed, A. Rasheed, M. S. Khan and A. K. A. Bhettani, Thermodynamic Study of Supermolecular Order in AqueousSolution of Poly (Vinyl Alcohol) *J. Chem. Soc.`Pak.* **12**, 221(1990).

124. A.Takada M.Nishimura, A. Koike and N. Nemoto, Dynamic Light Scattering and Dynamic Viscoelasticity of Poly (Vinyl Alcohol) in Aqueous Borax Solutions. 4. Further Investigation on Polymer Condition and Weight `Dependencies. *Macromolecules*, **31**,436 (1998).

125. B.Wang, S. Mukataka, M. Kodama and E. Kokufuta, Viscometric and Light Scattering Studies on Microgel Formation byç-raylrradiation to Aqueous Oxygen-Free Solutions of Poly (Vinyl Alcohol).*Langmuir*,**13**,6108(1997).

126. A.Hauge,B.Larsen and O.Smidsrod *Acta Chem.Scand*,**20**,183(1966).

127. Z.Wang,Q.Zhang,M.Kono and S. Saito, *Biopolymers,***34,**737 (1994).

128. E.D.T Atkins ,W.Mackie,K.D. parker and E.ESmolko,*J.polymer Sci.*part, lym. Lett,**9**, 311(1971).

129. O.Smidsrod,A.Haug and S.G.Whittington ,*Acta Chem.Scand,***26**,2563 (1972).

130. Flory, P. J.John Rehner, J., Statistical Mechanics of Cross-Linked Polymer Networks II.Swelling. *The Journal of Chemical Physics,* **11**, 521(1943).

132. K. Nakamura, E. Kinoshita, T. Hatakeyama and H. Hatakeyama, *Thermochim. Acta* **171**, 352 (2000).

133. A. I. Usov, *Russ. Chem. Rev.*, **68,** 957 (1999).

134. A. Ikeda, A. Takemura, and H. Ono, *Carbohydr. Polym.* ,**42** , 421 (2000).

135. G.O. Aspinall, The polysaccharides, Academic Press, New York, vol. 2 (1983)

136. T. W. Wong, L. W. Chan, S. B. Kho and P. W. S. Heng, *J. Controlled Release* ,**84**, 99 (2002).

137. D. F. Othmer and R. E. Kirk, Encyclopedia of Chemical Technology, John Wiley, New York 3rd., (1980).

138. C. K. Yeom and K. H. Lee, Characterization of sodium alginate membrane crosslinked with glutaraldehyde in pervaporation separation. *Journal of Applied Polymer Science* **67 (2),** 209 (1998).

139. M.Iza, S. Woerly, C.Danumah, S. Kaliaguine and M. Bousmina, Determination of pore size distribution for mesoporous materials and polymeric gels by means of DSC measurements: thermoporometry. *Polymer* **41(15)**,5885(2000).

140. P. J.Flory,. *Statistical mechanics of chain molecules*. Repr. ed. with corrections ed.;Oxford University Press: New York, (1989).

141. B. Amsden and N.Turner, Diffusion characteristics of calcium alginate gels. *Biotechnology and Bioengineering,* **65** (**5**), 605 (1999).