Surface science is a study dealing with the changes in physical or the chemical phenomenon occurring at the surfaces. It is known that surface phenomenon deals with molecules on surface. In simple terms it is said that evaporation is a surface phenomenon while the boiling of water is bulk phenomenon. Other different surface phenomena like adsorption, corrosion, catalysis, detergency, membrane processes [1, 4] etc., are seen in day to day life. Any modification of the surface or interphase usually leads to an increase or decrease in molecular interaction between the continuous phases. Surface phenomena can be purely physical in nature, or they may be accompanied by chemical transformations. Knowledge of surface phenomena in biology is also important. The aim of increasing agricultural productivity, developing the microbiological industry and increasing the potentialities of pharmaceuticals and cosmetics by imposing the qualitative and safety analysis is in demand. Hence, by making changes in the molecular structure, type to improve upon their properties and the possibilities of widespread utilization of these materials are a task that has attracted attention in research.

Research relating to the surface-active materials is been carried out for almost a century in past. When surface science is concerned, surfactants, a group of *surface active agents* or also called the *soft-matter*, come into the mind [5]. This part is just the overview of main features of common surfactant molecules aiming to bring about a theoretical background relating to their chemical nature and fundamental physical properties. Surfactant usually is the organic compound possessing the ability to radically alter the surface and interfacial properties, by lowering the surface tension (or interfacial tension) between two immiscible liquids, the liquid-gas (air) or between a liquid and a solid [6]. Surface tension is an effect at the surface of a liquid that makes the surface behave as an elastic sheet. In the bulk liquid, each molecule can interact in all directions with surrounding molecules due to various intermolecular attractive forces, while, in contrast, the molecules at the air-liquid interface experience only partial attractions with neighbouring molecules from the liquid interior (Figure 1). Hence, they do not achieve the same level of interactions as bulk molecules (there may be a small outward interaction between surface and air molecules, but as air is much less dense than the liquid, it is negligible). In other words, the molecules at the air-liquid interface exhibit energy excess compared to the bulk ones. Energy in the former case cannot be minimized further, as they interact only with the surrounding liquid molecules beneath the surface (Figure 1b). Therefore, the liquid shrinks itself till achieves the lowest surface area possible, in order to reduce the surface energy. The latter is defined as the surface tension of the liquid, which is expressed as a work done per unit area ($J \cdot m^{-2}$). Thus it can be simply said that the surface behaves in some aspects as if it was a stretched film or membrane under tension. The force along a line of unit length parallel to the film also corresponds to the γ (in $N \cdot m^{-1}$). When surfactants are added to water, they adsorb at the water-air interface to reduce the free energy of that specific phase boundary, due to their amphiphilic nature. The nature always favours the lower free energy, therefore, it is desirable.

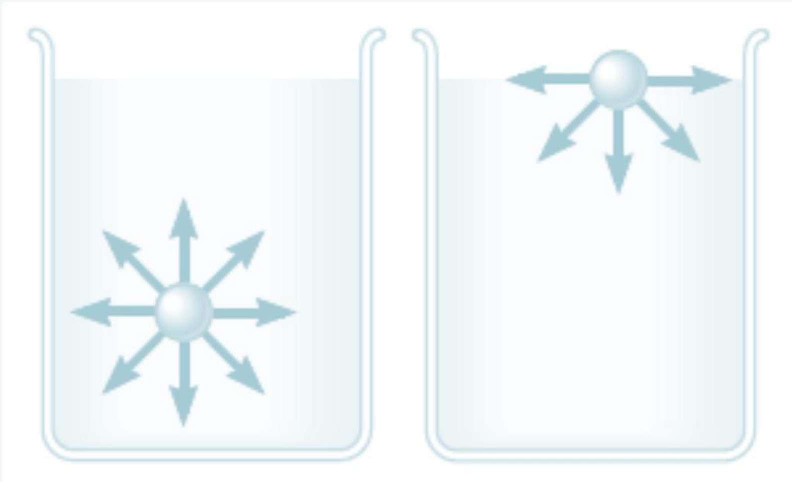


Figure 1: (a) A molecule within the bulk liquid interacts in **all directions** with other surrounding molecules. (b) A molecule at the surface experiences attractive interactions **only** with molecules from the **liquid interior.**

Surfactants being amphiphilic in nature contain water insoluble (hydrophobic) groups (their "tails") usually a straight hydrocarbon chain containing 8-18 carbon atoms and water soluble (hydrophilic) groups (their "heads"). The hydrophobic part of the surfactant molecule, soluble in oil (the non-polar solvents) but not very soluble in water and other polar solvents, is covalently attached to the polar functional portion, the so called hydrophilic part. Latter, on the other hand, is water loving but not very compatible with non-polar solvents. The interfacial water in the immediate vicinity of hydrophobic and hydrophilic surfaces plays a predominant role in various phenomena [7-9]. Due to the above two distinct groups, surfactant is also referred to as amphipathic, heteropolar or polar-nonpolar substances. Figure 2 shows a general representation of a surfactant molecule.

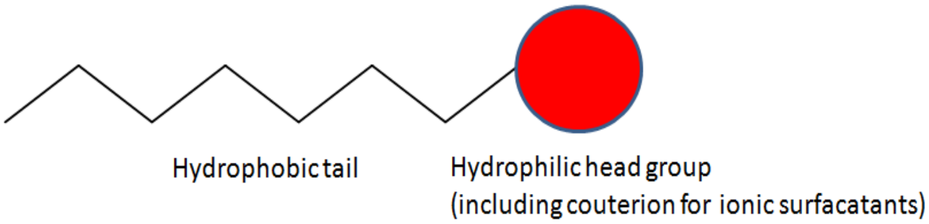


Figure 2: Schematic design for representation of a surfactant molecule.

Surfactants have great potential because of their amphiphilic nature together with the molecular structural diversity and spontaneous self assembling behavior [10, 11] in solution and on interfaces. Inspite being amphiphilic, a surfactant molecule is not fully compatible with either of the mediums. There is always a conflict between the affinity of head group and the tail. Generally the aqueous surfactant solutions are more likely to be favored, due to the formation of 3D, H-bonded network in addition to the attractive van der Waals interactions. Also, the amount of work required to expand the air water interface is relatively high. When the surfactants are added, they adsorb at the interface due to their amphiphilic character. Here, the hydrophobic part interacts weakly with water molecules whereas the hydrophilic heads interact strongly via dipole or ion-dipole interaction which makes the surfactant soluble in water. This collaborative action of surfactant, along with the 3D network of water, tends to throw the surfactant chain out of water (due to which these chains are referred as hydrophobic) and is responsible for the lowering of the surface tension. Thus, the amphiphilic nature forces them to adopt unique orientations in an aqueous medium to form organized assemblies which make them more promising as far as the applications are concerned. In aqueous surfactant solution, at well defined concentration, the abrupt changes occur in several physical properties such as electrical conductance and surface tension. This behaviour of surfactants can be explained in terms of formation of various organized assemblies like monolayers, micelles, vesicles (in an aqueous medium), emulsion and micro emulsion both in aqueous and organic solvents, and reversed micelles in organic solvents.

Surfactant solutions have attracted attention and are exploited because of their applications in both academia and industry. The solutions containing surfactants are amendable because of their tendency of having versatile role in different phenomenon like detergency, wetting, foaming, emulsification, solubilisation, adsorption, electrochemical sensing, as template, dispersions and in different industrial areas like chemical (mineral ore, fuel additives, paints, coatings and adhesives) and oil industry (petroleum), pharmaceuticals and bio-industries. Various applications of surfactants in production and processing of food, agrochemicals, personal care, laundry products, and in paper and photographic film industries are also found in recent past [12-20]. Thus, wide spectrum of physical, chemical, biological and medical applications is seen. Tremendous new developments in the extraction/pre-concentration techniques are also traced which brings new challenges to the extraction field to increase the efficiency, sustainability and versatility in the conventional procedures [21]. The search for new properties in the framework and to meet the societal eco-friendly requirements, there arise the demand of overcoming the extraction and other problems. Therefore, the research community is heading towards the challenges of the present century with continuous efforts to work upon the limits of the conventionally established extraction techniques. Surfactant based extraction is the beginning towards the application of potentially green procedures using surfactants.

Classification of surfactants

Surfactants being amphiphilic in nature can be classified into different ways. The hydrophilic part can be ionic or strongly polar group (such as ethylene oxide). Despite being known as head-group, the hydrophilic part is not necessarily placed at the end of hydrocarbon chain. More than one hydrophilic or hydrophobic group may be present in a surfactant molecule. Thus, on the basis of **nature of electrical charge** on the polar head group, surfactant can be classified into different groups.

When the head group carries a charge (positive or negative), they are known as ionic surfactants.

If the charge is positive, e.g. with a quaternary ammonium ion, it is called cationic. Typical cationic surfactants are alkyl amines, alkylimidazolines, quaternary ammonium compounds, ethoxylated alkyl amines and esterified quaternaries. Cationics represent a small and specialized part in cleaning product market.

Representative example is **CTAB ($CH_3(CH_2)_{15}N^+(CH_3)_3\ Br^-$)**

If the charge on the head group is negative, surfactant is called anionic surfactant. **Charged groups** (may be linear or branched) like sulfonates, sulphates, phosphates or carboxylates may be present. Anionic surfactants are quite sensitive to water hardness and are least expensive. **SDS ($CH_3(CH_2)_{11}SO_4^-Na^+$)** is an example of anionic surfactant.

A non-ionic surfactant has no charge groups in its head. Typical alkyl ethoxylates, alkyl phenyl ethoxylates, alkanediols, alkyl mono- and disaccharides, ethoxylated alkyl amines, ethoxylated alkyl amides, fluorinated linear alkyl ethoxylates, etc., are non-ionic in nature. They are not sensitive to water hardness. Non-ionic surfactants offer greater stability and flexibility than many anionics. They rank after the anionics in terms of industrial importance.

Polyoxyethylene alcohol $C_nH_{2n+1}(OCH_2CH_2)_mOH$ is the example of a non-ionic surfactant.

If the surfactant carries two oppositely charged groups, it is termed zwitterionic (amphoteric) surfactant. It works depending upon the pH of the solution. It can act as anionic surfactant in an alkaline solution whereas the cationic surfactant in an acidic solution and show the zwitterionic form around the isoelectric point. They form very small base to the society. They show good compatibility with other surfactants.

Dodecyl betaine $C_{12}H_{25}N^+(CH_3)_3CHCOO^-$, example of zwitterionic surfactant.

Not only the hydrophilic group can be modified, but the hydrophobic portion can also be of different nature and length. Generally the hydrocarbon chain can be medium to long chain (>C8), may be linear or branched and saturated or unsaturated. Alkyl benzenes or alkyl aromatics are the usual ones. Fluorocarbon or partially fluorinated chains, silicon chains and polycyclic structures can additionally be found in literature.

Based on molecular structures, surfactants are also divided into various classes such as gemini surfactants, bolaform amphiphiles, block copolymers, bio-surfactants among others.

Different Properties/Phenomenon shown by Surfactants

Surfactants when present in solution show different phenomena viz micellization, clouding, adsorption, spreading, wetting, solubilisation, emulsification etc. They can be used as models for biological studies, as electrochemical sensors and many more. Also, different special properties are often applied to surfactant solutions, e.g the hydrophilic-lipophilic balance (HLB), the aggregation number (*Nagg*), phase inversion temperature (PIT) and kraft temperature. Depending upon these properties the abilities of surfactants are easily classified.

Present thesis is mainly focussed on three important phenomena (***micellization, clouding*** and the ***morphological transitions)*** involved when the surfactant molecules are present in aqueous solution with and without additives.

Micellization

Surfactants possess the limits to how much they can lower the surface or the interfacial tension. In aqueous surfactant solution, at well defined concentration, the abrupt changes occur in several physical properties. This concentration is known as ***critical micelle concentration*** or ***cmc*** [22, 23]. It is the minimum concentration at which surfactant monomers begin to form micelles appreciably. *cmc* can be determined by various physico- chemical methods as shown in Figure 3 [24-27]. Due to these abrupt changes, the micellization phenomenon was suggested as the anomalous behaviour and explained in terms of formation of organised assemblies by McBain and Swain [28]. However, the *cmc* is a narrow concentration range and not a fixed value.

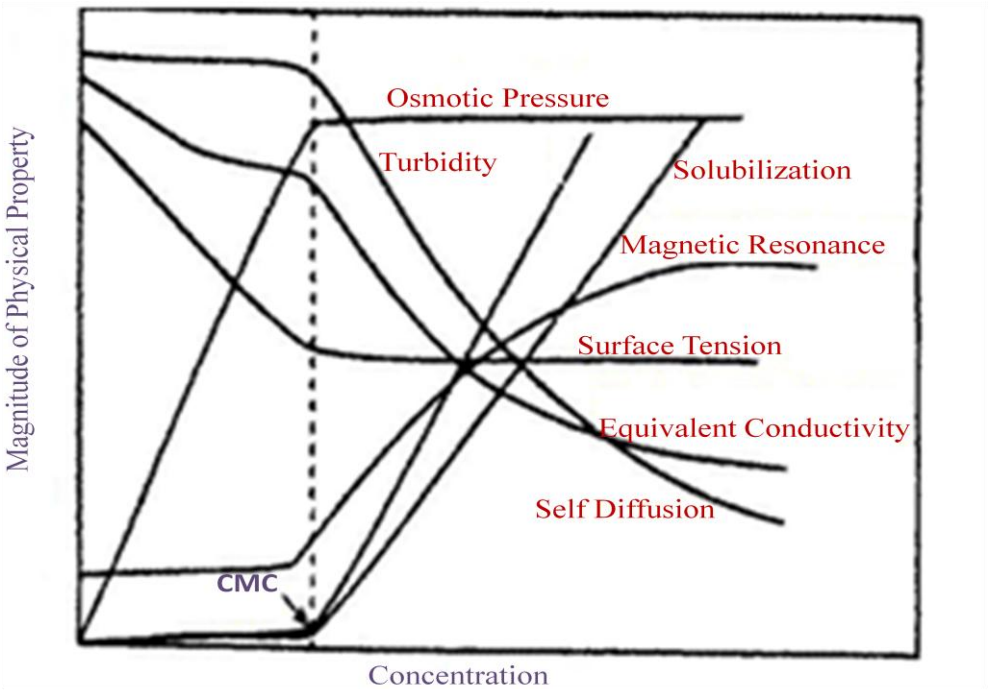


Figure 3: Different available methods to find cmc.

Surfactants when dissolved in aqueous medium, initially they get adsorbed on the surface resulting in the stable monolayer. After certain concentration, (*cmc)* the strong adsorption followed by the formation of bulk aggregates takes place. In aqueous solutions, at *cmc*, these aggregates are in dynamic equilibrium with the monomers. As they are short lived, they rapidly disassemble and reassemble which makes difficult the exact determination of shape and aggregation number. There arises a competition to balance adsorption and complete mixing due to thermal motion of the molecules resulting in the lowering of surface tension. In an organized system, monomer arranges itself in a particular manner to adopt unique orientations, wherein the hydrophobic hydrocarbon chains are oriented towards interior of the micelle and the hydrophilic head groups are in contact with aqueous medium (shown in Figure 4).

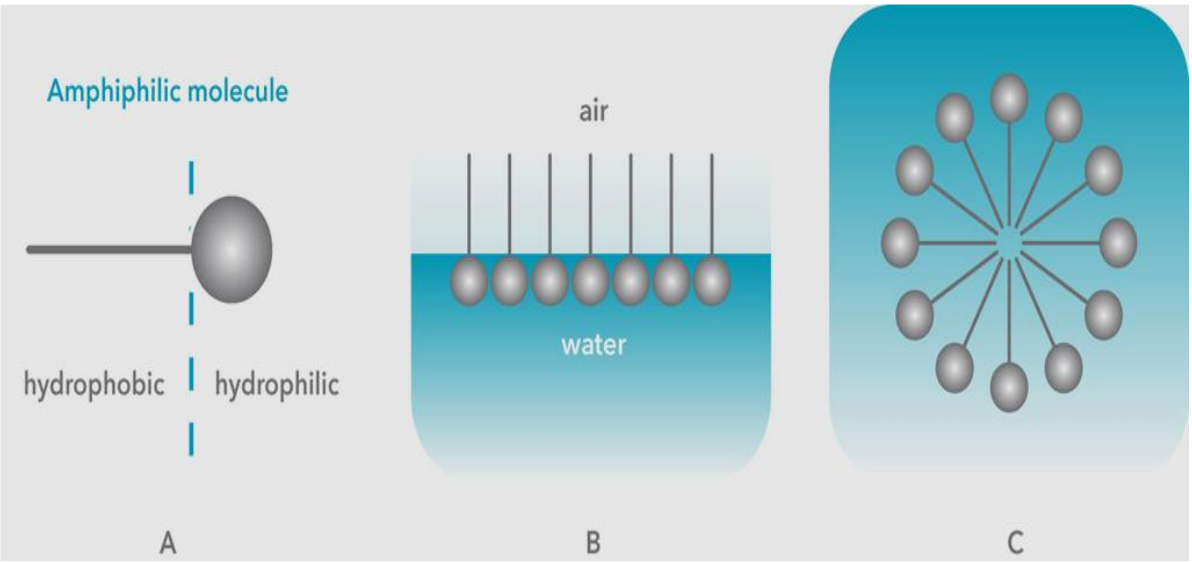


Figure 4: Arrangement of monomers in aqueous solution giving unique orientations.

The spontaneously formed aggregates may contain many surfactant molecules (approx 40-200) whose shape and size are governed by various factors. The aggregates so formed are energetically more favoured than the complete solubilisation in either of the phases. If the aqueous sample is not subjected to any external force, spherical aggregates are more promisingly formed as they occupy minimum surface area for a given volume near the *cmc*. Different morphological aggregates can be found under different conditions. There are two factors (Figure 5) governing the micellar shape: i) the steric force of repulsion between two like charged head groups; and ii) cohesive force of attraction between two monomeric alkyl tails or the packing curvature related to Mitchell- Ninham parameter ($P=V/a_0l_c$, where V and l_c are the volume and length of the alkyl part, respectively and a_0 is the head group area of a typical surfactant) [29]. The value of P depends on: i) optimal head group area (a_0)

that indirectly depends on the amphiphiles (molecular architecture), ionic strength, temperature/ pressure and the solvent, ii) the volume of alkyl chain (*V*) and iii) the critical chain length (l_c). The *V* and l_c can be calculated by empirical equations given by C Tanford [30], while a_0 can be measured experimentally as reported by Lantzsch *et al.* [31]. Due to the dehydration of counter ion and the surfactant head group, the counter ion condensation takes place and is responsible for various shapes of the micelle. The *P* increases due to condensation of various counter ions with a simultaneous decrease in the value of a_0.

The formation of various surfactant micro structures (e.g. rod like micelles, vesicles, lamellar phase or precipitates) and their dependence on critical packing parameter is shown in the Table 1.

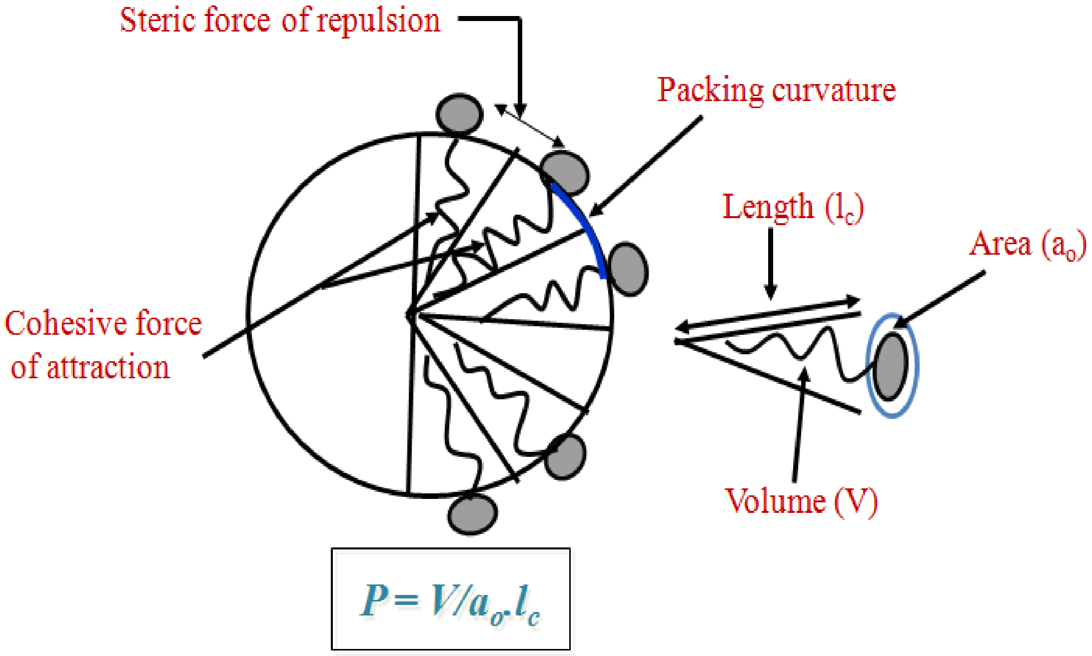
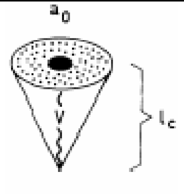
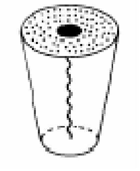
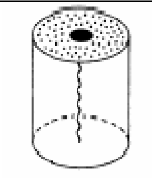
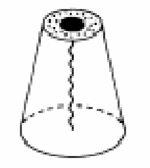


Figure 5: Various factors governing the micellar shape

Table 1: Dependence of shape on critical packing parameter **($P=V/a_0l_c$)**

Effective shape of the surfactant molecule	**Value of Packing parameter (P)**	**Aggregate morphology (Geometry of micelle)**
 Cone	< 1/3 (0.33)	Spherical micelle
 Truncated cone	1/3-1/2 (0.33-0.5)	Ellipsoidal/cylindrical micelle
 Cylinder	1/2-1 (0.5-1.0)	Rod like, vesicles, bilayer micelle
 Inverted (truncated) cone	>1	Reverse micelle

Solubilisation

Another interesting property of surfactants is their ability to enhance the aqueous solubility of a compound which otherwise is insoluble in aqueous, non-aqueous or in both medium. The phenomenon driven by the hydrophobic interactions is referred to as solubilisation. Due to the amphiphilic nature and the spontaneous self assembling behavior, surfactants possess versatile applications in solubilisation of the insoluble substrates. It becomes interesting to see how an additive at different micellar solubilisation sites can influence physical properties and the morphology involved therein. The amphiphilic characteristics of surfactants, past long, have extensively been utilized in eco friendly solubilisation of organic compounds in water, mobility of drugs in aqueous and lipid media, probing of biological systems, synthesis of nano-materials, detergency applications etc [32-34]. Thus the key property of micelles is to enhance the solubility of organic substances in aqueous solutions by providing multiple sites (Figure 6) of interaction where solutes can partition according to their hydrophobic or polar character.

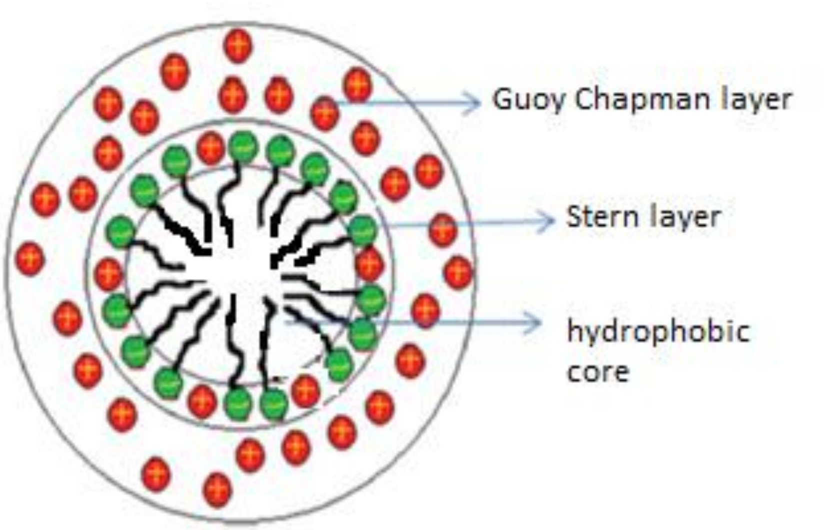


Figure 6: Various micelle solubilisation sites

Clouding

Recent developments in the description of interaction of charged colloidal particles with short range attractive forces have led to the interesting findings including metastable liquid-liquid phase separation and the formation of dynamically arrested morphologies [35-37]. Clouding is the physical change occurring in the amphiphilic surfactant solutions on heating. Due to this, phase separation takes place into two isotropic liquids at a particular temperature. Generally the solution behaviour of two types of surfactant (ionic and non-ionic) is in sharp contrast with respect to influence of temperature. Non-ionic surfactant solutions (e.g. *CiEj* type) cannot withstand elevated temperature and undergo clouding followed by phase separation into two isotropic liquids, surfactant lean and surfactant rich phases, at a well defined temperature known as ***cloud point (CP)*** [38].

Clouding, an important behaviour shown by nonionic surfactant solutions is also known as lower consolute behaviour or coacervate phase behaviour. *CP* can be lower consolute solution temperature (LCST), the temperature above which the two phases appear or upper consolute solution temperature (UCST), below which the two phase region appears as can be seen in Figure 7.

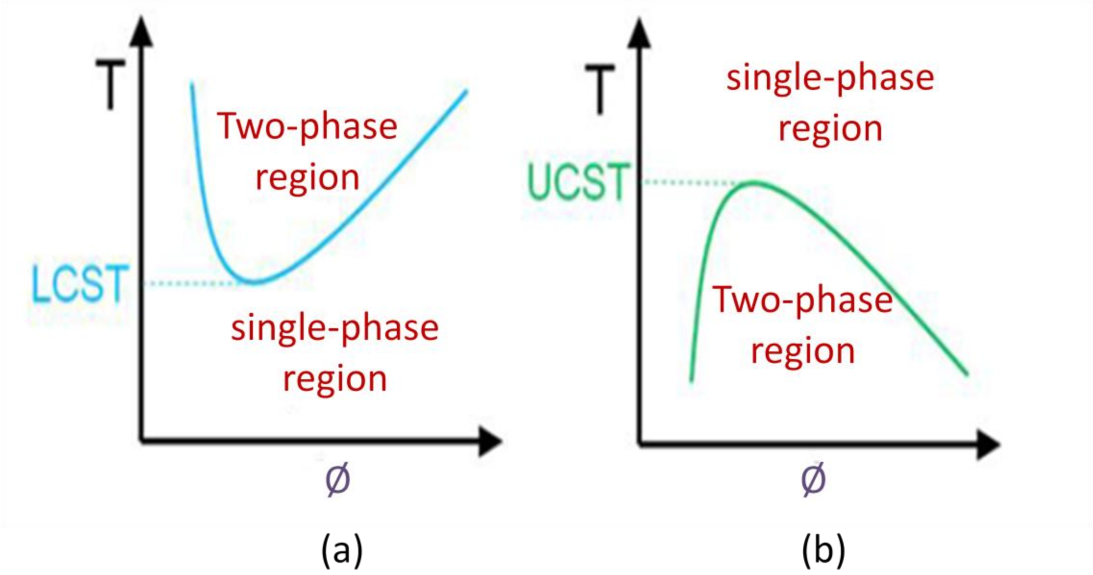


Figure 7: Temperature v/s surfactant volume fractions

A number of applications are reported for the CP phenomenon in diverse fields, [39-42] but the mechanism by which it occurs is not yet clear and still a source of controversy among different groups [43]. Many speculations have been suggested by different groups for the clouding in non-ionic surfactants. It is ascribed to an efficient dehydration of hydrophilic portion of micelles at higher temperature conditions. The Langer-Schwartz theory [44] predicts that the nucleated phase may appear as a cloud of small droplets that grow slowly beyond the critical droplet size or it may form as an isolated droplet that rapidly grow to a very large size. The analogy is drawn to surfactant solution in which liquid-liquid immiscibility occurs above LCST or CP. These micelles attract each other and form clusters [45] on approaching CP. Earlier, the phase separation was attributed to the micellar growth, the micellar coacervation, or the changes in poly (oxy ethylene) chain conformations with temperature [46-48]. The roles of oscillation in the critical concentration and of micellar growth as mechanisms for the clouding phenomenon are still topic of debate [49-51]. Another group proposed that clouding phenomenon is due to the interaction of non-ionic surfactant micelles via an attractive potential whose well-depth increases with temperature [52]. Using a lattice gas theory, it has also been shown that CP arises from a sudden increase in rotational entropy caused by rapid breaking of H-bonds between water and surfactant heads [53]. In recent reports, it has been proposed that the formation of the connected micellar network or strongly orientation dependent interactions [39,54] between water and micellar head groups could be responsible for the clouding phenomenon. The value of CP depends on the structure and concentration of the surfactant and the resulting hydrophobicity in presence of additives. Many studies are devoted to study the mixed micelle system as well as the effect of additives on the solution behaviour of the non ionic surfactants [55-66]. It is reported that a progressive dehydration takes place when the salt is added to the nonionic surfactant solution resulting in a smaller effective headgroup area provoking a shift in CP to lower temperature. Thus, change in micelle morphology also takes place. Effect of electrolyte depends on the interactions between the monomers in the surfactant micelle. It is found that micelle growth in such surfactants is due to two factors: increasing aggregation number and increased entrapped water in case of electrolyte addition. Many a times the transition from nonionic to ionic micelle is also demonstrated. Moreover, it is also well established that the addition of an ionic surfactant increases the CP of their non-ionic counter parts. Valaulikar and Manohar have demonstrated that the increase in CP can be described in terms of the surface charge per micelle, which is responsible for electrostatic repulsion between the micelles [67]. Clouding may also occur with the change in pressure or due to the presence of appropriate additives. A study of the transition from spherical micelles to wormlike micelles to vesicles (micellar growth) in non-ionic aqueous system with strong electrostatic interactions, and subsequent network formation is also studied using Cryo-TEM showing the first direct evidence for the existence of connected topology [57].

In the past, it was assumed that clouding and phase separation is not possible in aqueous ionic surfactant solutions due to electrostatic repulsion between the charged micelles. In ionic surfactant solutions, water-headgroup interractions are also expected to be stronger due to ion-dipole interactions making difficult for H-bonds to break on heating: the ultimate cause of clouding in case of non-ionic surfactants. In the case of anionic surfactants, the cloud point was first reported by Yu and Xu [68] for the surfactant tetrabutylammonium tetradecyl sulfate ($B_4NC_{14}S$) obtained by mixing the equimolar amounts of the quarternary ammonium salt, TBAB and sodium tetradecyl sulfate ($C_{14}SNa$) in water. Further, experiments were also conducted to examine whether phase separation phenomenon was the property of $B_4NC_{14}S$ or is due to the TBA^+ or ($C_{14}S^-$) ion alone. It was found that cloud point phenomenon was due to the behavior of $B_4NC_{14}S$ and not the property of TBAB or $C_{14}SNa$. It was found that CP decreases with increasing surfactant concentration. The micellization and phase equillibria in aqueous solutions of cationic quaternary ammonium bromide surfactants (alkyl tri-methyl-,-ethyl-,-propyl-,-butyl-,-pentyl-ammonium bromide) was also investigated as a function of alkyl chain length, electrolyte concentration and temperature. But no phase separation phenomenon was reported with head groups containing lower alkyl chains [69]. Instead, a large isotropic phase was observed in triethyl and tripropylammonium bromide. The change in head group from tri-propyl to tri-butylammonium in a cationic surfactant causes the appearance of clouding on heating. The phase separation was also observed for tetradecyltripentylammonium bromide. Thus, it was concluded that with solutions of alkyltributylammonium bromides presence of a large hydrophobic headgroup, is responsible for clouding [70-73]. Clouding and phase separation was also reported with the solutions of cationic surfactants erucyl-bis(hydroxyethyl)-methylammonium chloride in the presence of hydrophobic counterions such as tosylate or salicylate [74]. In contradiction to above results, no clouding was observed with tetrabutylammonium dodecanoate [75], tetradecanoate, octadecanoate, docosanoate or tetracosanoate [76] up to 98°C. Other conventional anionic surfactants (*e.g.*, SDS) having inorganic counter ions, are not prone to clouding. A few studies with ionic surfactants in presence of high salt concentration, salt free aqueous solution of certain ionic surfactant with large head group or large hydrophobic counter ion such as tetra-*n*-butylammonium perfluroalkanoate and some mixed cationic and anionic surfactant solution showing clouding phenomenon were reported in recent past [77-88]. There have been only a limited number of investigations of such ternary systems and the electrolyte was always presumed necessary to suppress the electrostatic interactions. Detailed studies of SDS in presence of simple inorganic salts are vast and can be found in literature. In contrast to the inorganic counterions, symmetrical quaternary cations are essentially nonhydrated and the positive charge is buried in paraffin shell due to which the unusual phenomenon can be expected with these cations. Subsequent studies with number of inorganic, organic and quaternary bromides with SDS in presence or absence of different additives in combination were performed to generalize the well observed clouding phenomenon in ionic surfactants. It was found that only a few quaternary bromides (TBAB, TBPB, and tetra-*n*-amylammoniumbromide, Am_4NBr) were found effective in producing CP that too in a very limited concentration range. Thus, it was proposed that CPs were found when the alkyl moiety (R) was quite large (e.g., butyl and above), whereas the lower number of carbon chain salts failed to give show the phenomenon. Also, the nature of headgroup and the effect of counterion on the micellar surface seem to be of prime importance to observe clouding. In SDS, the CP occurred at a lower concentration of quaternary phosphonium salt when compared to that with quaternary ammonium salt. The clouding phenomenon of sodium linear alkylbenzene sulfonates in presence of various quaternary organic salts has also been reported. [89-91] It has been found that, CP can be tuned with [surfactant] and [counterion]. An increase/ decrease in CP with the increase in [surfactant] or the increase in [R_4N^+] has been reported [84, 86, 92]. Keeping above views in mind, few researchers have studied variety of systems in context of clouding in charged micellar solutions in presence of different additives [93, 94]. Since most of the additives studied have 3D structure and are comparatively bulky, their incorporation in the headgroup region play an important role depending upon the available volume of the surface charge [85].

This unusual behaviour was then explained in light of van der Waals attractive forces, dehydration and linking of micelles. Looking at above observations, it was intimated that clouding phenomenon in anionic surfactant solution can be correlated with the presence of butyl chain either in the head group or counter ion. These butyl chains may penetrate into the surface layers of two adjacent micelles [68]. Also, with the increase in alkyl chain the micellar interactions were more favoured due to increased hydrophobic interactions [82] with the breaking of structure of water resulting in CP at lower [quaternary salt].

Till here it was the mixed system wherein R_4N^+ was added externally in the anionic surfactant solution. With such systems, there is a disadvantage of having the presence of unknown amount of NaBr which hinders to know the exact role of added quaternary counterion. The formation of NaBr in the solution can complicate the interpretation of final CP data. Also, in some cases the concentration of the added inorganic counterions was quite high.

To remove the extraneous effect of Na^+, new surfactants having quaternary counterion are also synthesized which showed clouding in binary aqueous system. Solution behaviour of surfactants (tetra-*n*-methyl ammonium dodecyl sulfate, TMADS; tetra-*n*-ethyl ammonium dodecyl sulfate, TEADS; tetra-*n*-propyl ammonium dodecyl sulfate, TPADS and tetra-*n*-butyl ammonium dodecyl sulfate, TBADS synthesized from SDS and respective R_4N^+ salt has been studied. However, the clouding could only be seen in TBADS. The tetrabutylammonium tetradecyl sulfate (TBATS) also gives clouding on heating. This shows that not only the heating, but other factors like presence of large alkyl moiety of the counterion, plays an important role in the solution behaviour of ionic surfactants. Many studies are devoted to the clouding of TBADS in presence/absence of additives [95-102] with hazy view about the mechanism of clouding.

In most of the above studies TBA^+ ion was driven from an added salt or was the counter ion furnished by the surfactant. The quaternary alkyl bromide ion (R_4N^+) possesses four alkyl chains for interaction with the ionic head group. It may be expected that all four butyl chains of TBA^+ would go towards micellar core. But, due to the geometrical constrain they orient in only two possible directions: one towards the bulk water phase and other intercalating in the micellar core [100, 103]. The former butyl chains may link micelles together. The increased temperature causing dehydration of head group and hence the micellar surface, makes the interaction between the ionic head group and the R_4N^+ to be more effective. This results in pseudo non ionic micelles which are responsible for clouding. However, all micelles are not expected to involve in the process of linking. It is also proposed that steric restrictions would not allow all the dissociated TBA^+ to house in the volume available at the micellar surface [96]. Therefore, few TBA^+ could be available in the bulk aqueous phase. At low [TBA^+] in the bulk water, the entropy of mixing of such TBA^+ throughout bulk phase overwhelms the finite driving force to assemble, making aggregates no more than metastable.

It has been proposed by Vlachy *et al* [104] that the organic counter ion should strongly interact with the ‘soft’ sulfate head group resulting in a fairly strong ion-pair close to an uncharged dipolar head group. Further TBA^+ would like to stay near the micellar head group region also because of hydrophobic interactions. As a result formation of hydrophobic aggregates is expected which do not dissolve in the bulk solution. The aggregates may phase separate with the removal of water molecules still sticking to the aggregate surface. The increase in temperature may cause the removal of above sticked water of micellar surface and play a role in appearance of clouding. Therefore, it seems that a symmetrical organic counter ion is the major driving force for ‘soft’ surfactant head group such as sulfate or sulfonato.

Detailed morphological transition resulting due to heating remains nearly unexplored on the molecular level. A fair discussion regarding morphological aspects for the clouding phenomenon of non-ionic surfactants can be found in recent review [38, 43].

Different kinds of assemblies can be transformed in response to variations in environmental factors. Generally, for nonionic surfactants aggregation mainly is induced by three driving forces: hydrophobic interactions, hydration structures surrounding the headgroups and the hydrogen bonding. Among these three too, the hydrophobic interactions provide the largest contribution. It is also postulated for that the hydration forces in the case of non-ionic surfactant decrease as the temperature increases resulting in a decrease in number of water molecules around head group [105,106]. According to this assumption, the P will change resulting into different predicted structures as shown above. From a quantitative point of view, P cannot perfectly predict the formation of all structural types, but it can explain the formation of aggregates qualitatively. Strey *et al* has also confirmed this experimentally, using SANS [107]. Thus, the explanation of CP in non ionic surfactants is generally accepted to be a decrease in hydration of the head group and increase in effective attraction between head groups on adjacent micelles. Based on the observations from the simulations molecular dynamics, this is well established [108,109]. Tiddy *et al* have also reviewed the phase behaviour of series of nonionic surfactants in water by optical microscopy over the temperature range of 0-100°C including various phase diagrams [110]. The complex phase diagrams were discussed as the multiple mechanisms acting together showing the complexity of the phenomenon. However, very little is known regarding the morphologies present in ionic surfactant solutions below and at/above the CP.

Thus, inspite of the clouding phenomenon easily seen in the non-ionic surfactants, main focus of the present work will be on the ionic surfactants because phenomenon is not well understood. Clouding in ionic surfactant appears slowly than non-ionic ones. Therefore, such systems could be used to study micellar morphology very near to the CP. Also, there exists an unresolved ambiguity concerning the relation between micellar growth and phase separation in case of ionic surfactants. Phase separation or clouding in ionic surfactants has been the subject of many experimental and theoretical works. Inspite of various intelligent propositions, no experimental evidence is available regarding the morphology of micelles when the system approaches the CP. In case of ionic surfactants, dehydration of head groups, depletion of the electrostatic interaction among alkyl sulfate anions, and micelle-micelle interaction via bridging with TBA^+ (mere speculations), have been proposed as the causes of clouding phenomenon [76,98].

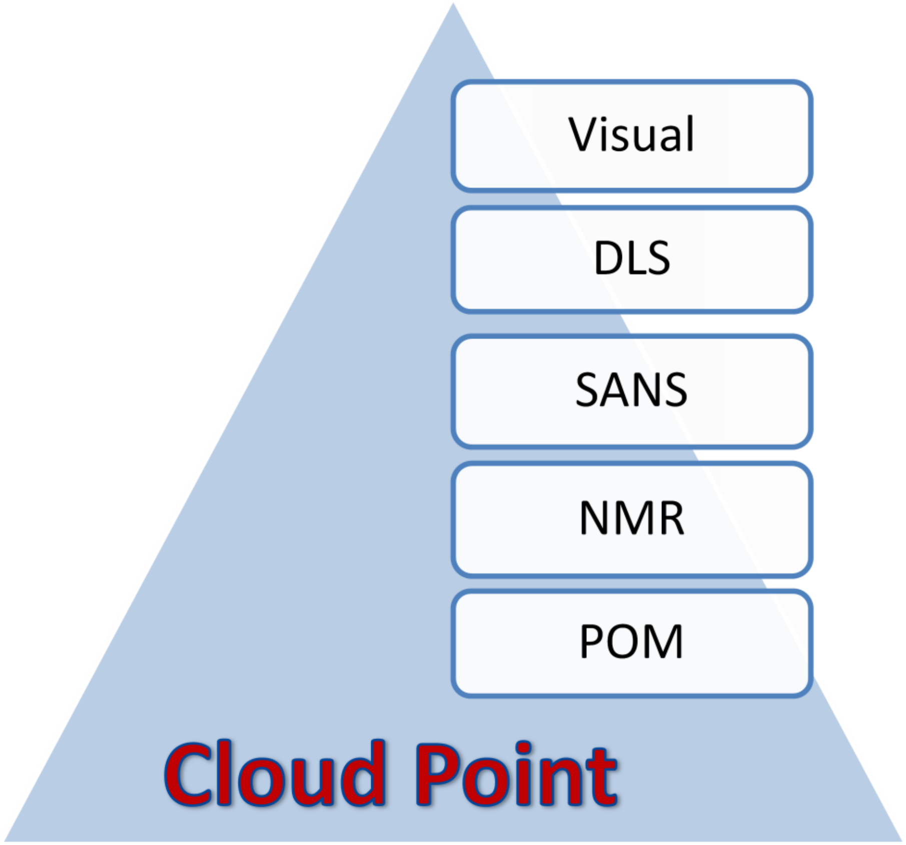
For ionic surfactants, it is established experimentally that the formation of rod like micelles of ionic surfactants is enhanced by the addition of electrolyte and/ or decreasing the temperature, showing that salt addition and increase in temperature work oppositely with respect to micellar growth. As temperature plays an important role in morphological transitions [111,112] it is important to study the effect of temperature on the ionic surfactant solutions with respect to CP. Usually the transition from a higher order aggregate to a lower order state on increasing the temperature takes place [113-115]. Among the ionic surfactants, micellar growth behaviour on heating is common only for some cationic surfactants mixed with oppositely charged surfactants/hydrotropes [112, 116, 117]. Studies of the temperature induced micellar growth are so far rare for single anionic surfactant system. Most of the time discussion regarding the mechanism of clouding phenomenon in charged micellar solutions ended with a hazy picture [76, 98, 99, 101, 118-120]. Therefore, some key questions need to be addressed in order to understand the rationale behind the morphology and solution behaviour.

The clouding in a surfactant solution can be considered as the solubility limit at or above which phase separation takes place. Therefore, the stabilities of the surfactant systems in solution phase with respect to temperature prior to their multifold uses need to be studied. Clouding phenomenon is widely exploited for the extraction and pre concentration of various analytes. This approach was originally introduced by Watanabe *et al* [121]. Since last two decades the cloud point extraction (CPE) has gained many fold interest over other extraction techniques for the separation of environmental [122-130] and biological [131, 132] samples of interest. Later on, it was extensively exploited as a primary isolation step in purification of proteins [133]. Paleologos et al. compiled an excellent overview on the fundamentals, methodology and applications of the CPE technique [134]. Till date, mostly CPE is used for preconcentration of analytes in form of their hydrophobic complexes, using the non-ionic surfactant systems [135]. The CPE method has usually limited capabilities for the extraction of thermally-labile compounds if the surfactant solution has a high CP or if much higher temperature than the CP is needed to be maintained for a long time in order to allow maximum extraction [136-139]. This problem can be solved by using surfactants that have CP near room temperature (RT). Unfortunately, the application of ionic supramolecular assembly-based separations has been hindered in practice, as the phenomenon rarely occurs for charged molecular aggregates [76].

Conditions leading to clouding in ionic supramolecular systems are, therefore, interesting from theoretical and practical points of view. Recently, there was a comprehensive review on using supramolecular solvents in the extraction of organic compounds [140]. The extraction methodologies are known as *cloud point extraction methodologies* (**CPEM**). CPE has the potential to replace hazardous solvent extracting systems and, therefore, beneficial for the point of view of green chemistry approaches. It also offers a simple, rapid, sensitive, and inexpensive alternative to other separation or pre -concentration techniques based on organic solvent. Thus, CPEM can find its best application in: the trace analysis of environmental and biological samples, preparation of samples, purification and their preconcentration that has been major challenges for analytical chemists; the pre-concentration, determination and separation of metal ions in water and food samples; the determination of drugs and other bioactive compounds and developing sensors for water hardness.

Many conventional extraction methodologies are found in literature but CPEM can find its profound implication in green chemistry because of the ability surfactants giving CP, to concentrate a variety of analytes with high concentration factors (in the surfactant rich phase), enhancing the detection limit of the instrument. Also, from the safety and cost points of view it can serve as an excellent alternative to conventional sample concentration methods that use large amounts of toxic and flammable organic solvents.

The aim of this work is to study the effects of the surfactant hydrocarbon chain, polar head group part, counterion, additives, surfactant concentration and temperature on the clouding of the anionic surfactant aqueous solution. An up to date literature on the research problem addressed in the present thesis has been compiled in this chapter. Various quaternary anionic surfactants have been synthesized and characterized for the study of clouding behavior and the morphological studies. The synthesis and the materials together with the methodologies adopted, are compiled in Chapter 2. The clouding behavior (CP data) and thermodynamic parameters of clouding are compiled in chapter 3. Various studies are conducted to collect the information regarding the morphological transitions taking place when the surfactant solution approaches the CP. The experimental evidences along with the qualitative arguments are compiled and discussed in chapters 4 and 5 to explore the obscure mechanism of clouding. The last Chapter 6, deals with the variation of CP in presence of drug or the drug intermediate. A few pre-concentration and the metal extractions are also tried in order to have an idea of the potential of the quaternary anionic surfactants.



Over all Clouding Studies in Quaternary Anionic Surfactants