Chapter- 1

INTRODUCTION

1.1 Surfactant Science and Technology:

The term surfactant is a blend of "Surface Active Agent". Surfactants are usually amphiphilic organic compounds (normally possessing a hydrophobic tail and a hydrophilic head) which allow them to change the interfacial properties of liquids in which they are present. The science behind this is a multitude of other splendid, interesting and useful properties is the science of surface active agents (surfactants) or surfactant science.

Revolutions in the field of chemical industry in recent years have undoubtedly posed a question to scientists, engineers, regulators and managers if they are up to date with the latest technologies, as these things necessarily have some impact on their work. Consideration should be made in the huge increment in the publishing of scientific and technical journals that have paralleled with an apparent divergence into fields of "pure" science and "applied" science and technologies where the first one corresponds to the general advancement of human knowledge with no particular practical aim in mind and the other one has its research directed by some anticipated application, not always, sometimes profit-oriented though. This sort of growing contrast in purpose more than the study of surface and colloid science, in respect to surface activity and surface active materials have been demonstrated. Variations can be found even in the nomenclature being used in discussing materials showing surface activity, depending on the context of discussion. It comes of no surprise then, when one appears complex and confused regarding surface-activity and surface-active agents, or surfactants provided that he/she is not keenly involved in it on their everyday lives. Contemplation on the impact of surfactant science in general, and emulsions, dispersions, foaming agents, wetting agents, and other related compounds in particular, in our everyday lives; and the clear image that comes into our mind reveals the magnitude of impact, these areas of chemistry and chemical technology have made through to our lives. Interest in increasing performance like detergency, household and personal care products has also led to research in mixed surfactant systems. Other commercial interests have also influenced the development in surfactant science. For example in the 1970s, during the oil crisis, new methods of enhanced oil recovery, such as micro emulsions, were heavily investigated. Scientific curiosity has also driven surfactant research into areas such as organization of surfactant molecules into interesting, shapes and structures, all with unique properties. Surfactants have ever been the subject of investigation into the origins of life; meteorites containing lipid-like compounds have been found to assemble into boundary membranes and may be an interstellar pre-biotic earth source of cell membrane material. The functional divergence of academic and applied research have doubled attacked the science and technology of surfactants. The increasing concentration of academic research in surfactants on highly purified homogeneous material [mostly confined to few materials such as Sodiumdodecyl sulfate (SDS) or Dodecyltrimethylammonium bromide (DTAB)] and classy analytical techniques. The application of such knowledge which is under investigation, to more complex practical materials and processes is often less than obvious, and can sometimes be misleading too. The irony is that real surfactant systems are mostly made up of mixed chemical isomers, contaminants, and added materials that has power to totally bring change in the effects of a given surfactant on a system.

Although surfactant science is now a reasonably mature discipline, there is still room for new molecules designed for specific purposes and new applications (such as nanoparticles synthesis and more diverse and environmentally friendly consumer products). These new materials have spurred on the quest for improved molecular models, computer simulations and improved structure-activity relation-ships. Slight modification of the molecular structure with respect to conventional surfactants leads to a rich morphology of structures that are being explored by increasingly more sophisticated techniques and in turn, enhancing our under-standing of their properties at a molecular level.

Before moving on to the specific aspects of the chemistry of surface-active materials and surfactant action, it may be useful to have some idea regarding the historical background of surfactant, their synthesis and applications that have evolved through the years, about parallel development of surfactant and the pro-vision of new surfactant technologies in various areas of the world.

1.2. Historical Background

The discovery of soap predates recorded history, going back perhaps as far as six thousand years. Soap like material found in clay cylinders during the excavation of ancient Babylon was evident that soap making was known around 2800 B.C. Inscriptions on the cylinders said that fats were boiled with ashes. Later records from ancient Egypt, the Ebers Papyrus, and a medicinal document from about 1500 B.C. described combining animal and vegetable oils with alkaline salts to form soap-like materials used for treating skin diseases as well as for washing.

According to an ancient Roman legend, soap got its name from Mount Sapo, where animals were sacrificed. Rain would wash the mixtures of melted animal fat, or tallow, and wood ashes down into the clay soil along the Tiber River, where people found the mixture helped clean clothes. The Germans and Gauls were also credited with discovering a substance called soap which was made of goats' tallow and ashes that they used to tint their hair red [1]. The Romans developed the process for themselves at a later stage, as did the Arabs and over the last millennium the production and use of soap has grown widely all over the world. The alkali metal soaps have been used for at least 2300 years. Their use as articles of trade by the Phoenicians as early as 600 B.C. has been documented. The recipe for making soap was relatively unchanged for centuries with American colonists collecting and cooking down animal tallow (rendered fat) and then mixing it with an alkali potash solution obtained from the accumulated hard wood ashes of their winter fires. The mixtures of fats, ashes and water were boiled, in which fat was saponified to the free fatty acids, which were subsequently neutralized. The first well-documented synthetic (non soap) materials which were employed especially for their surface active properties were the sulfated oils. Sulfonated castor oil, originally known as "Turkey red oil" was produced by the action of sulfuric acid on the castor oil. It was introduced in the late nineteenth century as a dyeing aid and is still used in textile industries today.

The chemistry of soap manufacturing stayed essentially the same, when the first synthetic detergent was developed in Germany in response to a world War I– rela-ted shortage of animal and vegetables fats for making soaps. Those materials were short-chain alkyl naphthalene sulfonates prepared by the reaction of propyl or but-yl alcohol with naphthalene followed by sulfonation. The product simply known today as detergent which showed good wetting characteristics and used as cleaning agent. In the late 1920s and early 1930s, the resulting products of sulfonation of long chain alcohols were sold as the sodium salt [2].

Similarly in the early 1930s, long chain alkyl aryl sulfonates with benzene as the aromatic group was discovered in the United States. At that time, both alcohol sulfates and alkyl aryl sulfonates were common in use but with lesser impacts on the general surfactant or detergent market. The alcohol sulfates had been almost completely replaced by the alkyl aryl sulfonates on cleaning basis by the end of the World War II. The first "built" detergent (containing a surfactant/builder combination) was introduced in the U.S. where the surfactant is a detergents product's basic cleaning ingredient while the builders (i.e. phosphate compound) helps the surfactant to work more efficiently. Secondary olefin sulfates were also extracted and had large scale production in the United Kingdom. Later on, the propylene tetramer (PT) based alkyl benzene sulfonates (ABS) took a steadfast position in the world market due to their easiness in manufacture and flexibility.

1.3. Surface Active Agents (Surfactants)

1.3.1. Introduction of Surfactants

A surfactant is organic molecule that, when present at low concentration in a system, has the property of adsorbing on to the surfaces or interfaces of the system and altering to a marked degree the surface or interfacial free energies of those surfaces [3]. A surfactant is composed of two parts, the hydrophilic and hydrophobic, rendering them amphiphilic in nature. The hydrophobic part usually consists of a hydrocarbon chain and the hydrophilic part, also called the head group, can be ionic or a highly polar nonionic part.

Surfactant molecules are composed of a polar head group that likes water and a non polar tail group that dislikes water, thus contributing to an intrinsic duality in their molecular characteristics. Despite their mutual antipathy, the head and tail groups of the surfactant cannot leave one another because they are covalently connected. The dilemma faced by these molecules is resolved in nature by the intriguing phenomenon of molecular self assembly, wherein the amphiphiles self assemble into three dimensional structures with distinct and separate regions com-posed of the non-polar parts and the polar parts, having minimal contact with one another [4]. The behavior of surfactants in aqueous solution is determined by their tendency to move their hydrophobic part away from the solution and their hydrophilic part towards the solution. This dual tendency is responsible for the adsorption of surfactant at interface and for the formation of such aggregates as micelles. Surfactant molecules adsorb at the water/air interface with their hydrophobic groups away from the water and their hydrophilic groups in the solution. A consequence of this is that some of the water molecules at the interface will be replaced by hydrocarbon or other non-polar groups. Since the interaction force between water molecules decreases, adsorption of surfactants at the interface results in a reduction in the surface tension of the solution.

The surfactants are classified after the nature of the polar head group, such as nonionic, anionic, cationic and amphoteric. Because of their amphiphilicity, surfactants are inclined to adsorb to interfaces to lower the free energy. One other essential surfactant property is the ability to form stable associated structures above a certain concentration, called the critical micelle concentration (cmc). The aggregation process depends both on the surfactant type and the solution (e.g. ionic strength, P^H) in which they are dissolved. The molecular aggregates are known as micelles; ionic surfactants form small micelles in low ionic strength solutions because of the electrostatic repulsion between adjacent head groups and entropic penalty of confining the counter ions close to the micelle. The micelle radius is approximately equal to the length of the hydrocarbon tail. Non ionic surfactant can form both spherical micelles and other geometries depending on temperature and the relative size of the hydrophobic and hydrophilic part [5]. The characteristics of solution containing surfactants, such as detergency, wetting, emulsification, dispersion and foaming, have many practical applications in daily life and industry.

The existence of surfactant molecules in the form of self-assembled aggregates was first suggested by Mc Bain in 1913 based on his studies on how the conductivity of a solution of soap molecule changes with the concentration [6]. However, surfactant can be natural or synthetic origin. Surfactants from natural origin (vegetable or animal) are known as oleo-chemicals and are derived from sources such as palm oil or tallow. Surfactants from synthetic origin are known as petro-chemicals and are derived from petroleum.

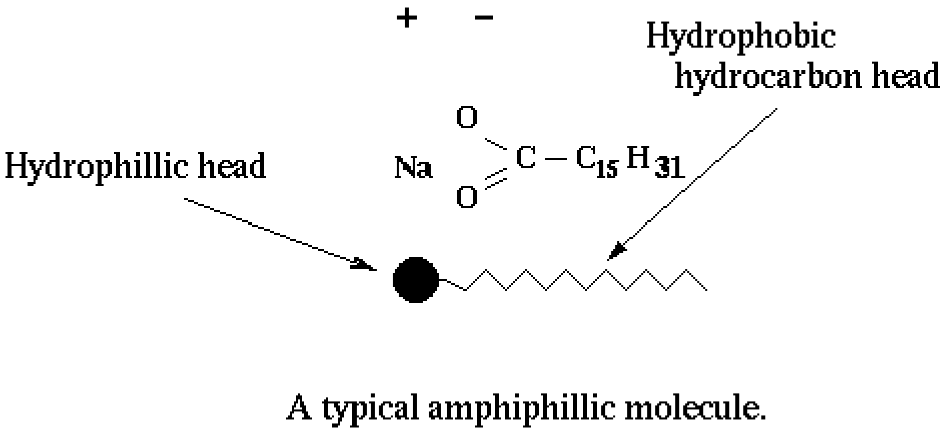


Figure 1. Structure of an amphiphilic surfactant

1.3.2. Mixed Surfactant system

Mixed surfactant systems have been for a long time one of the favorite areas for experimental studies on interfacial and bulk properties of surfactant. When surfactant are added together in water, several physicochemical properties of the mixed system compared to those of the single surfactant are changed due to the fact that there is a net interaction between the amphiphiles, i.e. due to non-ideal mixing. It is well known that many amphiphilic self-assemblies and interfaces, biological or synthetic-based, consist of surfactant mixtures. The molecular structure of the surfactant (head groups and tails), the presence of additives (salt, co-surfactant) and experimental variables (P^H, temperature) can be manipulated in order to induce changes in interfacial activity and in intra-and inter aggregate forces. The mixed system almost invariably yields enhanced interfacial properties (e.g. decreased cmc, higher surface-activity) with respect to the individual surfactant, in what is termed synergism [7]. The optimization of mixture of surfactants in aqueous solution is an important part of the formulation of many commercial cleaning products, so mixed surfactant systems are encountered in nearly all practical application of surfactant. Due to the natural polydisperity of commercial surfactants, resulting from impurities in starting materials and variability in reaction products during their manufacture [8]. Hence, one has the inherent difficulty preparing chemically and isomerically pure surfactant.

Surfactant mixtures are of considerable interest for numerous technical applications and are much favored from the view point of economy and performance when compared to the use of single surfactants. They are less expensive than isomerically pure surfactants. The latter often arises from the deliberate formulation of mixtures of different surfactant type to exploit synergistic behavior in mixed systems or to provide qualitatively different types of performance in a single formulation. The performance of mixed surfactant systems is often superior to that of a single surfactant system and practical formulation often require the addition of surfactant additives to help control the physical properties of the product to imp-rove its stability. Hence, it is essential to understand how surfactants interact in the mixtures [9].

Mixed surfactant systems are also of great theoretical interest. A mixed micellar solution is a representation of a mixed micelle, mixed monolayer at the air/solution interface and mixed bilayer aggregate at the solid interface. In solution containing two or more surfactants, the tendency of aggregated structures to form is substantially different from that in solution having only pure surfactants. Such different tendency results in dramatic change in properties and behavior of mixed surfactant compared to that of a single surfactant [10]. Especially, mixing two surfactant ions of opposite charge, cationic/anionic surfactant mixtures show remarkable different physicochemical properties and behavior. For example, synergistic effects seem to be negligible for mixtures of nonionic surfactants. Ionic/nonionic mixtures, on the other hand, do show appreciable synergism [11]. However, cationic/anionic surfactant mixtures exhibit the largest synergistic effects such as reduction in critical micelle concentration and surface tension [12]. Mixtures of surfactants can exhibit synergistic gains compared to the parent surfactant in both surface and bulk properties [13]. This is particularly true when there are attractive interactions between the surfactants, as is the case in mixture of anionic and cationic surfactant. Mixtures of nonionic surfactants tend to behave ideally while ionic surfactant can exhibit departure from ideality [14]. From a fundamental point of view, the mixtures of cationic (Cetyltrimethylammonium bromide) - nonionic surfactants (Polysorbate 20) are more interesting because they often exhibit a highly non ideal behavior. Adding a non ionic surfactant into a cationic surfactant micelle can reduce the electrostatic repulsion between the charged surfactant heads and greatly facilitate mixed micelle formation causing the cmc to decrease. The cmc decreases to a certain minimum and then increased with the temperature displaying a U-shaped behavior [15].

1.3.3. Classification of Surfactants

There is a broad range of different surfactant types, each with unique properties and characteristics. Depending on the type of the charge and the nature of the ion, surfactants can be classified on the following classes:

i) Ionic surfactant
ii) Non-ionic surfactant

Ionic Surfactants

The head group of an ionic surfactant can be ionized in an aqueous solution. Depending on the nature of ionization, ionic surfactant can be further categorized in a number of subcategories as follows:

i) Anionic surfactant
ii) cationic surfactant
iii) Amphoteric surfactant

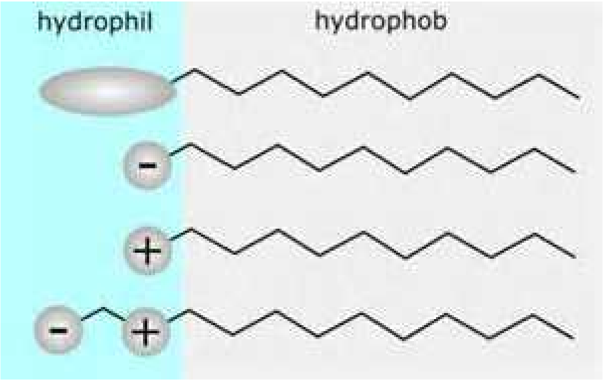


Figure 2. Diagrammatically different type of surfactants

Anionic surfactant

Anionic surfactants are those which carry a negative charge (anion) on at least one part of the molecule. The hydrophilic part of the molecules can be a carboxylate, sulphate, sulphonate or phosphate. They are generally non-toxic and most widely used surfactant. They are mainly used in detergent formulation and personal care product. Some examples of anionic surfactants are alkyl benzene sulfonates (detergent), fatty acid (soaps), di-alkyl sulfosuccinate (wetting agents) and sodiumdodecyl sulfate [16].

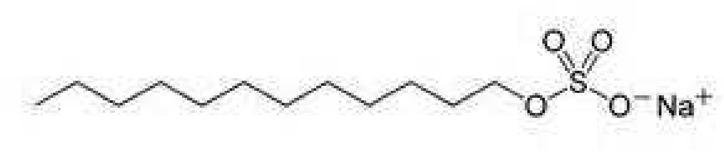


Figure 3. Molecular structure of sodiumdodecyl sulfate (SDS)

Cationic surfactant

Cationic surfactants are dissociated in water into a negatively charged ion and a positively charged ion. And the hydrophilic head is positively charged (cationic). These surfactants are in general more expensive than anionic, because of high pressure hydrogenation reaction to be carried out during their synthesis. Typical cationic surfactants are alkyl amines, alkylimidazolines, quaternary ammonium compounds, ethoxylated alkyl amines and esterified quaternaries. Cationic remain a small, specialized part of cleaning product market [17]. They are widely used for treatment of synthetic fabrics and protein molecules of which have negatively charged sites.

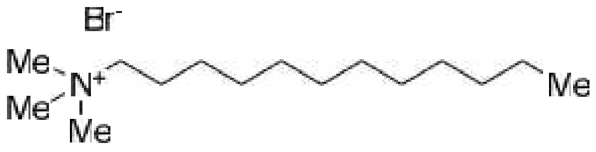


Figure 4. Molecular structure of Dodecyltrimethylammonium bromide (DTAB)

Amphoteric surfactant

When a single surfactant molecule exhibits both anionic and cationic dissociation, it is called amphoteric or zwitterionic [16]. Zwitterionic surfactants carry a positive charge on a cationic site and a negative charge on an anionic site. The charge of the molecule changes with the P^H value of the solution and show a zwitterionic form around the isoelectric point. They are generally quite expensive and consequently their use is limited to very special applications such as cosmetics, baby shampoo and daily cleaners. Some examples are amino acids, imino acids, betains and lecithins etc.

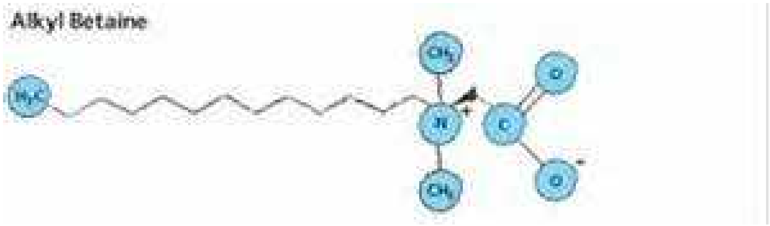


Figure 5. Molecular structures of Alkyl betaine

Non-Ionic Surfactants

This class of surfactants are characterized by the lack of groups that can be easily ionized. They do not ionize in aqueous solution because their hydrophilic group is of a non-dissociable type, such as alcohol, phenol, ether, ester or amides. A large proportion of these nonionic surfactants are made hydrophilic by the presence of a polyethylene glycol chain obtained by the poly-condensation of ethylene oxide [16]. Anionic are gradually replaced by milder non-ionic surfactants in detergent products (milder to environment). As the large laundry products change from powders to liquids, nonionic surfactants offer greater stability and formulation flexibility than many anionic. Some examples of non ionic surfactants are penta-oxyethylenedodecyl ether ($C_{12}E_5$), n-octylβ-D-glucoside(OG) and Ethoxylated alkylamides.

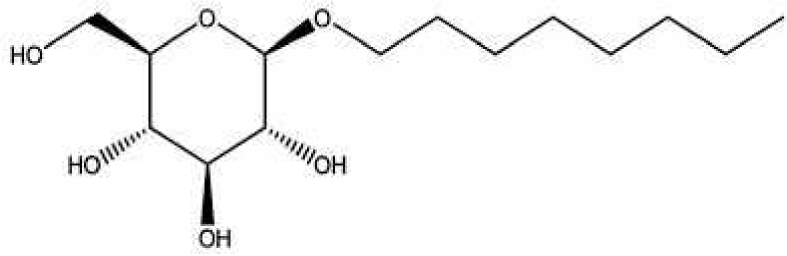


Figure 6. Molecular structure of n-octyl β-D-glucoside (OG)

1.3.4. Critical Micelle Concentration

When surfactant are in solution above a certain concentration, called the critical micelle concentration (cmc), they tend to undergo spontaneous self association into ordered structures called micelles. The critical micelle concentration indicates usually a narrow range of concentration separating the limits below which most of the surfactant is in the monomeric state and above which virtually all additional surfactant molecules enter the micellar state [18]. Micelle formation is so important in the chemistry of surfactant solution since it is at cmc that abrupt changes in their solution and performance properties occur. Several studies have shown that the cmc of single surfactant and their mixtures can easily be determined by measuring a physical property of surfactant solution against its concentration [19-21]. Critical micelle concentration is usually indicated by an inflection point on the curve of the physical property plotted against solution concentration.

Theoretically, cmcs of aqueous solution of binary mixtures of surfactant can be predicted from the knowledge of the cmcs of the single surfactant component assuming ideal mixing. The composition of the mixed micelles differed from that of pure surfactants because of their mutual interaction [22]. The interaction between the species present in the surfactant mixtures has been studies in the light of the regular solution theory of Rubingh [23]. It deals with the non ideality of the mixed systems based on several approximations [24, 25]. According to Rubingh [23], when two surfactants are mixed, the mixed cmc (cmc_{mix}) is given by equation (1)

$$\frac{1}{cmc_{\mathrm{mix}}} = \frac{\alpha_1}{f_1 cmc_1} + \frac{1-\alpha_1}{f_2 cmc_2} \qquad (1)$$

Where, α_1 is the stoichiometric mole fraction of surfactant 1 in the mixed solution, f_1 and f_2 are the activity coefficient of surfactants 1 and 2 respectively, and cmc_1 and cmc_2 are the corresponding critical micellar concentration for pure surfactants 1 and 2. If the mixed system behaves ideally then the activity coefficient of both surfactants will be equal to unity ($f_1 = f_2 = 1$) and equation (1) is reduced to Clint equation [26]:

$$\frac{1}{cmc_{\mathrm{mix}}} = \frac{\alpha_1}{cmc_1} + \frac{1-\alpha_1}{cmc_2} \qquad (2)$$

The ideality of mixing can then be estimated considering the difference between these values. Clint's theoretical treatment of mixed surfactants has been useful especially in comparing ideal and non-ideal behavior of mixed surfactant systems. Deviations from ideality are a function of the nature of interaction between the component surfactants which can be repulsive or attractive. Attractive interaction between surfactant mixtures may result in synergism, a case in which the fundamental properties e.g. surface tension reductions, critical micelle concentration (cmc) of the mixture are superior to those of the single surfactant.

Experimentally, the cmc is measured by many microscopic and macroscopic techniques. Usually the cmc of the surfactant are determined by the measurement of physicochemical parameters of their aqueous solution as a function of surfactant concentration. An excellent critical evaluation of the methods for determining cmcs is included in the comprehensive and compilation of cmcs in aqueous solution by Mukerjee and Mysels [27]. Among the experimental techniques routinely used for measuring mixed cmcs are surface tension measurement, conductivity, dye solubilization and light scattering. Other methods have also been demonstrated including calorimetry, kinetic approaches, cyclicvoltametry and oil-solution interfacial tension measurements. The most widely used technique for the determination of mixed cmcs employs conductivity (for ionic surfactants) and surface tension measurements [9]. The cmc is usually determined as the point of intersection of two lines that interpolate the experimental data for low and high surfactant concentrations. The cmc is sometimes determined as the point of maximum curvature of the plotted macroscopic property of the micellar solution (e.g. conductivity; or surface tension) as a function of surfactant concentration. The cmc is influenced by many external factors including temperature, pressure, p^H, ionic strength, and volume of the solution and also by the surfactant chemical structure such as the length of hydrophobic tail, head group area etc [28]. The cmc decreases strongly with increasing the hydrocarbon chain length of the surfactant because the critical chemical potential, $K_BT\log(cmc)$, decreases linearly with chain length, with each methyl group contributing about 2-3K_BT. The cmc of ionic surfactants (typically 10^{-3}- 10^{-2} M) is orders of magnitude higher than the one of nonionic amphiphiles (typically 10^{-5}-10^{-4} M). This is due to the smaller repulsion between the head groups in the non ionic case. The addition of salt decreases the cmc of ionic surfactants by up to an order of magnitude. This effect is due to the electrostatic screening caused by the salt ions, which reduces the repulsion between the ionic head groups. Critical micelle concentration is depen-dent on the balance of forces between electrostatic repulsion of charged head groups and attractive forces of alkyl chain length [29]. Repulsive interactions oppose aggregation and therefore increase cmc. Increase in temperature would enhance thermal agitation of ionic head groups. Thus, electrostatic repulsion is stronger leading to reduced aggregation and resulting in increased cmc.

The cmc values of nonionic surfactants depend on the length of both the lipophilic and hydrophilic parts of their molecules. The cmc decreases with increasing length of the hydrophobic moiety for a fixed hydrophilic group. Due to different structural consequences of intermolecular interactions caused by the different chain length of the alcohols, the cmc decreases sharply as the hydrocarbon chain length of alcohols become larger. Critical micelle concentration decreases as the non ionic surfactant mole fraction number increases. It has been reported that the synergism of solubilization in mixed micelle solutions decreased with increase in the mole fraction of the nonionic surfactant [30].

Also, cmc is a fundamental physicochemical property of a surfactant, often deter-mined by measuring the surface tension (γ), as a function of surfactant concentra-tion(C). The presence of hydrophobic impurities in a surfactant is shown by a minimum in the γ-logC plot. In a recent study comprising either single surfac-tants, mixed surfactants or surfactant admixed with another surface–active comp-onent, it is shown that existence of a minimum or a negative peak in the γ-logC profile may imply that the amphiphile is a mixture, but the absence of the neg-ative peak does not imply the absence of impurity or that the surfactant consists of only one component [31]. However, cmcs of mixed surfactants are also useful tools predicting the strength of interaction between them in comparison to the inte-raction of the single surfactant molecules before mixing. The importance of cmc for both single and surfactant mixtures therefore, is an integral part of the study of any surfactant system.

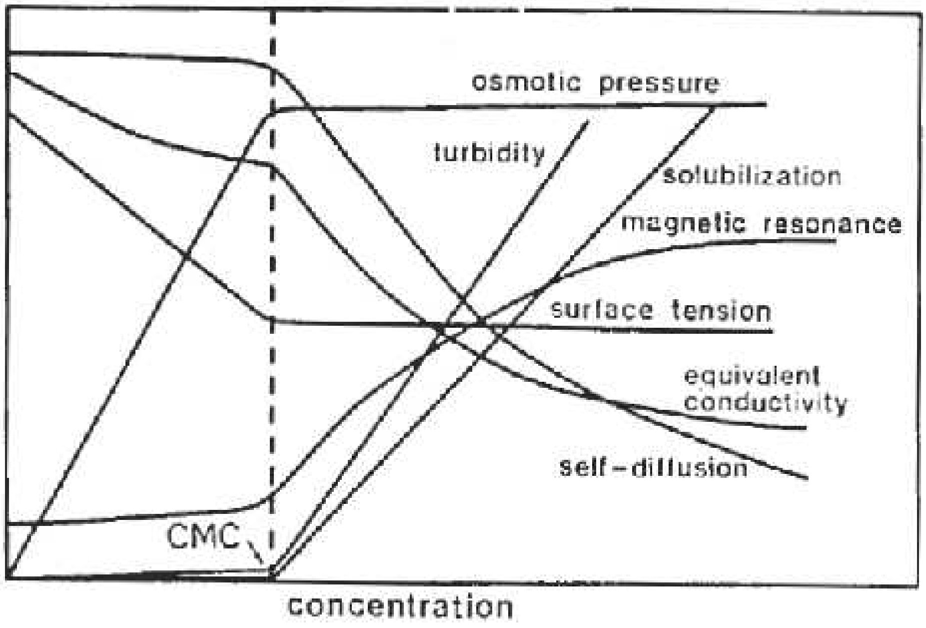


Figure 7. Change in concentration dependence of a wide range of physicochemical quantities around the critical micelle concentration

1.3.5. Factors Affecting the Micelle Formation and CMC

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. The rise of micelles is possible only above kraft temperature (T_k). This temperature is an important point in the phase diagram of solubility versus temperature. Below T_k, the solubility is so small that micelles cannot form.

In the case of ionic surfactant, the cmc decreases as the temperature increases because of the lowered hydration of the hydrophilic parts. Then the value of the cmc reaches its minimum and further increase in temperature is followed by increasing of the cmc due to disruption of the structured water surrounding hydro-carbon chains. The tendency of the cmc behavior in a particular temperature region is influenced by the balance between effects promoting and opposing micellization [32-35]. The cmc values of non ionic surfactants decreases with the increasing temperature [36-38]. Chen et al [39] presented the temperature dependence of nonionic surfactant of the PEO types and describes reaching the minimum of the cmc for not charged surfactants, as well. This minimum point was estimated at high temperature, around 50^0C. Above this temperature the cmc increases again.

Also the factors that reduce head group hydration at higher temperatures will also reduce energy increase caused by the structured water molecules around the hydrophobic portion of the surfactant molecule. The results from that scenario will be a reduction of the magnitude of the free-energy component attributable to the hydrophobic or entropic effect [G]. Such an effect will increase the “solubility”– or more accurately decrease the “insolubility”– of the tail in water, a result that is in opposition to micelle formation. Increasing temperature promotes growing of large aggregates up to a certain temperature, called “cloud point”. The phase separation is realized due to the lowering of number of hydrogen bonds between hydrophilic groups and water molecules [32].

The hydrophobic group the ‘tail’**:** The length of the chain of a hydrocarbon surfactant has been shown to be a major factor determining its cmc. It is known that the cmc decreases logarithmically as the number of carbons in the chain of a homologous series n_c increases. The relationship usually fits the Klevens [40] equation as:

$$\log_{10}(cmc) = A - Bn_c \qquad (3)$$

where A and B are constants specific to the homologous series under constant condition of temperature, pressure, and other parameters, and n is the number of carbon atom in the chain, C_nH_{2n+1}. The value of A is approximately constant for a particular ionic head group, while B is constant and approximately equal to $\log_{10} 2$($B \approx 0.29$-0.30) for all paraffin chain salts having a single ionic head group.

The nature of the hydrophobic part of charged surfactants leads to lowering of the cmc as the number of carbon atoms in the hydrocarbon chain increases. Higher number of carbon atoms increases the surfactant water repellence and due to this process, the cmc shifts to lower value. This effect has not been proved chains longer than sixteen carbon atoms. The analogous effect can be achieved by ben-zene ring introducing to the surfactant structure. On the other hand, modification of the hydrocarbon chain by introducing another hydrocarbon branch, double bond or a polar functional group into the structure of surfactant, as well as substi-tution of hydrogen atoms by ionic groups, lead to the increasing cmc. The interfa-cial tension and the cmc are caused by the nature of hydrophobic terminal groups [CF_3 or H-CF_2] [41, 42].

Hydrophilic part: Considerably, lower cmc values for nonionic surfactants comparing to the ionics are resulted in the fact that discharged surfactant do not need to carry out an electric work attached to the micelle formation. For non ionic surfactants of the polyoxyethylene types, the cmc increases with the molecule polyoxyethylene chain prolongation.

Most ionic surfactants with the certain chain length show very similar values of the cmc values [32, 33]. With higher number of ionized groups included in the surfactant molecules, the value of the cmc increases, due to the increase in the electric work required to the micelle formation [33]. The location of the ionic group in the micelle of surfactant itself affects its micellar properties.

Effect of a counter-ion nature: In connection with the electrolyte effect on the cmc, the effects of the counter-ion nature is strongly associated. The increasing degree of counter ion binding to a micelle due to their increasing polarity, counter-ion valence or decreasing hydrated radius [32,33], a decrease of the cmc and increase of the aggregation number occurs [43,44].

According to the Esposito et al [45], the aggregation behavior of anionic detergents is less sensitive to the nature of counter-ion than in the case of cationic surfactants. Since electrostatic repulsions between ionic groups are greatest for complete ionization, an increase in the degree of ion binding will decrease the cmc. For a given hydrophobic tail and anionic head group, the cmc generally decreases in the order:

$$Li^+ > Na^+ > K^+ > C_s^+ > N(CH_3)_4^+ > N(CH_2CH_3)_4^+ > Ca^{2+} \approx Mg^{2+}$$

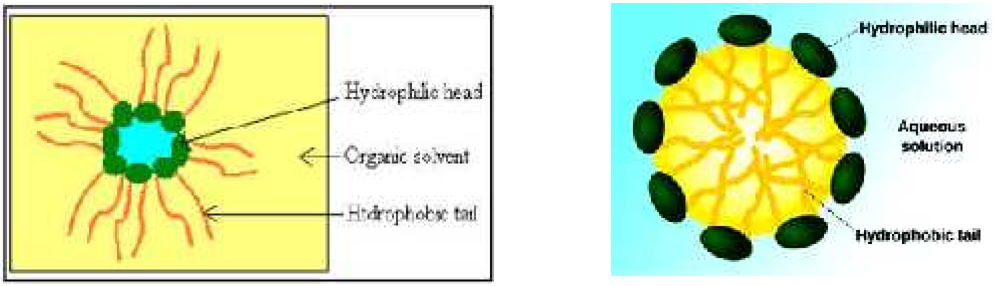
In the case of cationic surfactant such as Dodecyltrimethylammonium halides, the cmcs are found to decrease in the order: $F^- > Cl^- > Br^- > I^-$. In addition, varying counter ion valency produce a significant effect. As the counter ion is changed from monovalent to di and trivalent, the cmc is found to decrease rapidly.

Effects of additives in solution on cmc (Electrolyte addition): The electrolyte effect is mostly pronounced for ionic and less for nonionic and amphoteric surfactants. As the ionic power of solutions rises up, the cmc decreases and the transition from spherical to cylindrical shape along with the increase of the micelle aggregation number occurs. The decrease of the cmc values is ascribed to the releasing of counter-ions from hydrophilic parts of surfactants and also from the added electrolyte. The electrolytes dehydration activity is an important effect, which also lowers the cmc of ionic surfactants. Solutions of electrolytes remove the lyosphere of surfactant and as a consequence, ions become strongly hydrated. In addition, the effect depends on the type of counter-ion.

Already Klevens [46] in 1948 was engaged not only in the cmc value measuring, but also with the electrolyte effect on the cmc of soaps. He concluded that cmc decreases with the addition of an electrolyte to solution. As the other authors have also found, the value of the cmc decreases in the presence of an electrolyte in a micellar solution and this cmc reduction depends on the nature and concentration of cations [37, 45, 47].

1.3.6. Different Types of Aggregates

Micelle and Micellar Shape: In an aqueous solutions and above a critical micelle concentration (cmc), surfactant molecules aggregate and form roughly spherical structures called micelles, with the hydrocarbon tails pointing inward, towards the center of the sphere, and away from the water molecules while the hydrophilic or charged head groups are on the surface of the sphere and in contact with the bulk aqueous media. A micelle is formed by the repulsive forces among hydrophilic head groups and attractive force among hydrophobic tails.



(a) (b)

Figure 8. a) A schematic representation of a reverse micelle **b**) A general structure of a normal micelle

The presence of micelles was originally proposed by Mc Bain [6] who suggested that below the cmc most of the surfactant molecules are un-associated, whereas in the isotropic solutions immediately above the cmc micelles and surfactant ions (molecules) are thought to co-exist, the concentration of the latter changing very slightly as more surfactant is dissolved. However, the self-association of an amphiphiles occurs in a stepwise manner with one monomer added to the aggregate at a time. Micelles are closely spherical over a rather wide concentration range above the cmc. Indeed, Adam [48] and Hartley [49] first suggested that micelles are spherical and have the following properties:

i) The association unit is spherical with a radius approximately equal to the length of the hydrocarbon chain;

ii) The micelle contains about 50-100 monomeric units the aggregation num-ber generally increases with increasing alkyl chain length;

iii) With ionic surfactants, most counter ions are bound to the micelle surface, thus significantly reducing the mobility from the value expected from a micelle with non-counter ion binding;

iv) Micellization occurs over a narrow concentration range due to the high association number of surfactant micelles;

v) The interior of the surfactant micelle has essentially the properties as a liquid hydrocarbon. This is confirmed by the high mobility of the alkyl chains and the ability of the micelles to solubilize many water-insoluble organic molecules, e.g. agrochemicals.

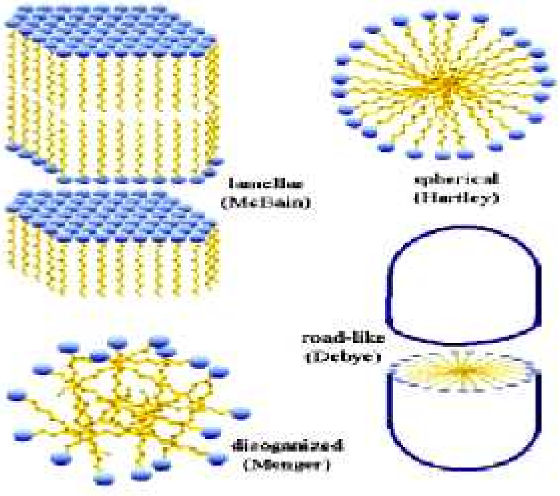
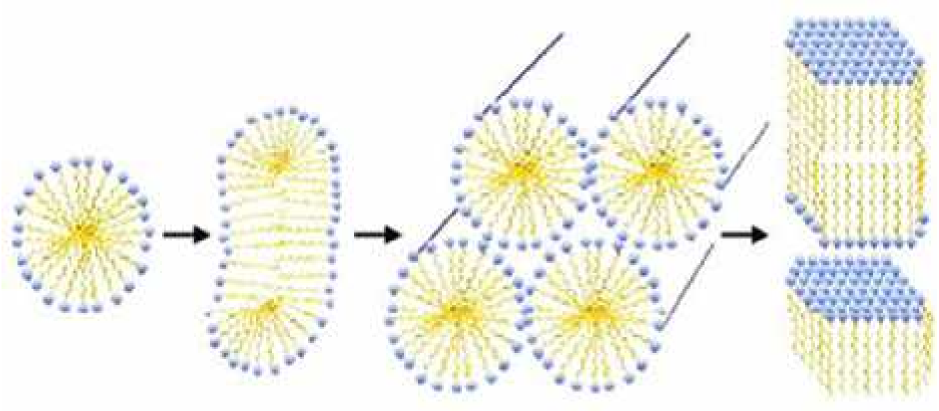


Figure 9. Different proposed structures of micelle

The shape of the micelle produced in aqueous media is of importance in determining various properties of the surfactant solution. At present time, the major types of micelles appear to be (i) relatively small, spherical structures, (ii) elongated cylindrical, rod like micelles with hemi-spherical ends (prolate ellipsoids), (iii) large, flat lamellar micelles (disk like extended oblate spheroids) and (iv) vesicles-more or less spherical structures consisting of bilayer lamellar micelles arranged in one or more concentric spheres. In general, the spherical form is accepted as the true representation of the micelle. With increasing surfactant concentration, the shape of ionic micelles changes in the sequence:

Spherical ⟶ Cylindrical ⟶ Hexagonal ⟶ Lamellar [50]



Spherical **Cylindrical** **Hexagonal** **Lamellar**

Figure 10. Change in micellar shape with respect to the change in surfactant concentration.

Vesicles: Vesicles are closed bilayer structures that enclose an aqueous pool and are surrounded by an aqueous solution [51]. Vesicles are not only interesting because they mimic biological membranes, they have recently also been used in applications such as drug delivery, nanotechnology and two dimensional crystallization of proteins. The geometry of vesicles as closed bilayer aggregates of flexible colloidal size allows their use as in vitro cell models for biochemical studies, as agents for the transport of substrates (gene delivery) and as nano-reactors for specialized chemistry, amongst other uses [31]. Both micelles and vesicles have amphiphilic molecules as building blocks and the issue is to tune the structures of these building blocks so that aggregates of the desired morphology and properties are obtained. Another important factor is the stability of the aggregates that are formed. For vesicles, the phase transition temperature of the bilayer is of particular importance. There is great demand for truly stable vesicles systems, strictly for thermodynamically stable vesicles. Since the early 1990s, experimental investigations on the phase behavior and aggregated structures of several mixed surfactant systems, in particular catanionic system, have revealed that equilibrium vesicle formation is a relatively common phenomenon [31].

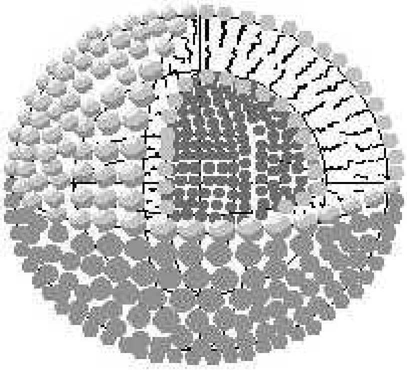


Figure 11. A schematic representation of a vesicle

1.3.7. Development and Uses of Surfactants

Mixed surfactant system have unique physicochemical properties that are different from those of their individual constituents, including lower critical aggregation concentration and higher surface activities which is important for detergency application [52, 53]. They have also been used as semi permanent wall coating for fused silica capillaries [54] in capillary electrophoresis (CE) applications or as pseudo-stationary phases in micellar electro kinetic chromatography (MEKC). The surfactants used in a multitude of industrial products, processes and other practical applications almost always consists of a mixture of surfactant because they are less expensive than isomerically pure surfactant and also they often provide better performance. Mixed surfactants are used widely in diverse applications such as enhanced oil recovery [55], mineral flotation [56] and drug carrier system.

Mixed surfactant systems such as mixtures of cationic and anionic surfactant can form several types of aggregated microstructures such as vesicles, lamellar phases, precipitates, spheres and rod like structures [57, 58]. The dynamic behavior of these vesicles systems could be important if they are to be exploited effectively in applications such as models for biological membranes, agents for fragrance and flavor encapsulation, selective separation aids vehicles for controlled release application and micro reactors for the preparation of inorganic nanoparticles [59]. Mixed surfactants are also used to synthesize template porous material incorporating titanium which is used for epoxidation catalysis [60]. Since a single surfactant rarely satisfies all requirement, mixed surfactants have been used for cosmetics, material fabrication and drug delivery among other areas [3, 61-63], industrial and pharmaceutical applications, waste water treatment, textile wetting, froth flotation and paper manufacturing [64]. Mixtures of anionic and cationic surfactant have been considered as one of an efficient way of remediation technique. There are the great advantages of using these mixed surfactants, for example, they can reduce interfacial tension (IFT), reach the lower cmc than the individual anionic or cationic surfactants [65] and also produce microstructures [66].

In addition surfactant mixtures are often more surface active than either pure surfactant and may be useful in different application such as rod like micellar solution have found use as drag-reduction agent in pipeline flow and stable vesicles phases are of potential use as micro reactors and agents for controlled drug release. Dilute liquid crystals can be utilized in the formulation of liquid detergent. The precipitation of mixed surfactant is useful in the quantitative analysis of surfactant [67].

1.3.8. Information of Surfactant under Study

Sodiumdodecyl sulfate [SDS]

SDS has the chemical formula $C_{12}H_{25}NaO_4S$ or CH_3-$(CH_2)_{11}$-O-SO_3-Na^+ and its structure is presented below. SDS has a polar anionic sulfate (hydrophilic) group at one end of their structures and a straight chain non polar (hydrophobic) region at the other end. The salt consists of an anionic organo sulfate consisting of a 12- carbon tail attached to a sulfate group, giving the material the amphiphilic proper-ties required of detergent [68].

SDS is a white or cream colour crystal, flake or powder primarily used as a surfactant. It is odorless compound having molecular weight 288.372. SDS is widely accepted to have a cmc of 8mM [27]-9.4mM [69]. It is used both for fundamental studies as well as in many industrial application [68]. It is a highly effective surfactant and is used in any task requiring the removal of oily stains and residues.

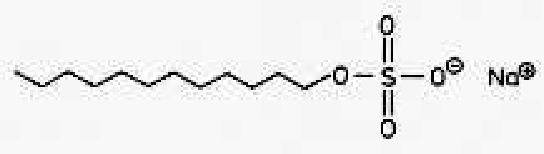


Figure 12. Chemical structure of SDS.

SDS has a wide variety of applications. Among them, major use of SDS is as a synthetic chemical surfactant for emulsion polymerization. It also has protein denaturing power [68]. Sodiumdodecyl sulfate is also used in the analysis of haemoglobin. Other major uses of SDS include, as a wetting agent and adjuvant in insecticides; as an emulsifier in the electro plating industry; as dispersant and penetrant in varnish and paint remover; as a whipping agent and surfactant in food and as a cleaning agent in a wide variety of personal care products such as toothpastes, shampoos and shaving cream-any products that requires a thickening effect and the ability to create a lather [70].

Dodecyl trimethylammonium bromide (DTAB)

The IUPAC name of dodecyltrimethylammonium bromide is dodecyl(trimethyl) azanium bromide. DTAB has the molecular formula $C_{15}H_{34}BrN$ and its structure is presented below. It is an odorless compound having molecular weight 308.3 and melting point 246.0 ^{0}C. DTAB is a white to slightly yellow powder, which should be stored in closed container in a cool dry place, primarily used as surfactant. DTAB has been reported to have a cmc of 14.5 [71].

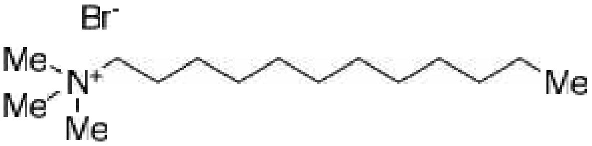


Figure 13. Chemical structure of DTAB.

It is a highly effective cationic surfactant used in daily life. DTAB type of compound is found in high concentration in industrial products like detergent industries etc. The charge on the head group of DTAB is positive that is why the surfactant is said to be cationic surfactants. Due to the positive charge of the head group, cationic surfactant strongly adsorb on the negatively charged surfaces such as fabric, hair and cell membrane of bacteria. DTAB has wide variety of application in industries and therefore, they are used as paint strippers, foaming stabilizers and bactericidal lotions. It is useful biochemical for proteomics research.

This cationic surfactant is used as emulsifier of rubber and asphalt. It is also used for disinfection of silkworm rearing room. Additionally, it can be used as anti-static agent of synthetic fibre, oil-field flooding fungicide and surfactant. Similarly, it can be used to produce dodecyltrimethylammonium bromite. DTAB is a single chain surfactant. It has been used in a study to assess the relation between counter-ion distribution and miscibility of counter-ions at the solution surface. This was deduced for surfactant mixtures containing common surfactant ion but different counter-ions [72].

1.4 Literature Survey of the Study

The micelle formation of the mixed surfactant in solution has been known to be affected by the temperature, pressure and various kinds of additives [73- 75]. Interactions between cationic and anionic surfactants studied by electrical conductance are very less in number [76,77]. Broad range of works was oriented on properties of systems consisted of conventional cationic and anionic surfactants [78-18], anionic dimeric and conventional cationic surfactants [77]. Zana et al [77] investigated the kraft temperature, cmc, micelle ionization degree of cetyltrimethylammonium in the presence of an anionic dimeric (Gemini) surfactant through electrical conductivity but not calculated the thermodynamic properties. The phase behavior and structures of mixtures of oppositely charged surfactant had been studied [58, 82-84]. For those studies, measurement of conductivity, cryo-transmission electron microscopy, time resolved fluorescence quenching and quasi-elastic light scattering were used.

Most applications of the mixtures of cationic and anionic surfactants included personal cleaning products, hair care and laundry aids [85]. Hines described, some the recent advances in the theoretical evaluation of micellization in mixed surfactant systems[85]. Thermodynamic properties of micellization of sodiumdodecyl sulfate in binary mixtures of ethylene glycol with water had been studied [86]. Investigated on the effect of formamide and other solvents, including dimethylsulfoxide and dimethylacetamide on the micelle formation of sodiumdodecyl sulfate was reported and observed the reduction of both critical micelle concentration (cmc) and mean aggregation number of sodiumdodecyl sulfate micelles upon the addition of formamide[87]. The cmc of the single surfactants and their mixtures was easily be determined by measuring a physical property of surfactant solution against its concentration [19-21, 88].

It was studied the aggregation behavior and thermodynamics of mixed micellization of Gemini surfactants with a room temperature ionic liquid in water and water-organic solvent mixed media [89]. It was studied the mixed micellization behavior of Gemini surfactants with some conventional surfactants in aqueous and aqueous polyethylene glycol (PEG) solutions at different temperature using conductometric and viscometric methods [90]. Precipitation of anionic surfactants [91-93] and mixtures of anionic/nonionic surfactants [94] had been previously successfully modeled. The behavior and physicochemical properties of mixtures of a highly branched cationic and sodium alkyl sulfate was widely studied [95-97].

The thermodynamic quantity known as the partial molar volume has proved to be a very useful tool in elucidating the interactions occurring in solutions. Studies of the partial molar volume have been used to examine the behavior of surfactant solution [98-101]. Effect of concentration, temperature and solvent composition on density and apparent molar volume of the binary mixtures of cationic-anionic (CTAB and SDS) surfactants in methanol-water mixed solvent media were studied [102]. The density data of sodiumdodecyl sulfate in the presence of cetyltrimethylammonium bromide in pure water and in methanol-water mixtures were found to be higher than the density data of sodiumdodecyl sulfate in pure water and in methanol-water mixtures had been observed [102]. The presence of cetyltrimethylammonium bromide with sod-iumdodecyl sulfate will naturally increase the density and decreases with increa-sing temperature were investigated [103]. At low concentration of sodiumdodecyl sulfate in the presence of cetyltrimethylammonium bromide, the apparent molar volumes were concentrated dependent. Such behavior had also been noticed by [104] while calculating apparent molar volume of alkylmethylammonium bromide where as irregular pattern of decrease in apparent moalr volume at low concentration of surfactant mixture were observed [102].

The interaction of CTAB with anionic polyelectrolyte, polystyrene sulfonate (PSS), had been studied by surface tension measurement [105]. The study indicated that the surfactant aggregates which wrapped up with PSS chains, and hydro-phobic interaction is an important factor in the bonding of the surfactants to PSS [106]. The surface tensions of several mixtures of SDS (sodiumdodecyl sulfate) and DTAB (dodecyltri-methylammonium bromide) was studied [12] and similar results were also found [53]. The properties of anionic-rich and cationic-rich mixtures of CTAB (cetyltrimethyl-ammonium bromide) and SDS (sodiumdodecyl sulfate) through conductometry and surface tension measurement was investigated and determined [107]. It was also further determined critical aggregation concentration (CAC), surface tension reduction effectiveness (γ_{CAC}), surface excess (Γ_{max}) and mean molecular surface area (A_{min}) from plots of the surface tension as a function of the total surfactant concentration [107]. Micellization of tetradecyltrimethylammonium bromide (TTAB) and sodiumdodecyl sulfate (SDS) in water-ethanol (ET) mice-llar solution with the weight percent of ET changing with the range 0-30 were studied [108] by means of surface tension and conductivity measurement.

The synergism in binary mixtures of surfactants had been studied [11,109-113]. Synergism of mixtures of surfactants increase with the degree of charge difference between them, which means the mixtures of anionic and cationic surfactants, presents the highest level of synergism. It was noticed that the most of the mixed cationic-anionic surfactant systems, precipitate at equimolar concentration at very high water content [67]. At non equimolar concentration, the mixture forms micelles with different sizes and shapes, closed bilayers vesicles and dilute lamellar phases. The formation of aggregates and their transformation are justified in terms of inter-action forces and surfactant geometry. These features were studied on the mixed system of cetyltrimethylammonium bromide-sodiumdodecyl sulfate [114]. The formation of water-soluble pseudo-nonionic complexes of anionic and cationic surfactants was studied [115]. The oppositely charged surfactant diminishes the surface charge density of the mixed micelle [116].

1.5 Objectives of Study

This dissertation work was carried out to study of interaction of cationic (DTAB) and anionic (SDS) surfactant in water and methanol-water mixed solvent media. The solution properties such as: density, conductance and surface tension of mixed surfactant are studied. Since the micellization behaviors of mixed surfactant are also studied through some properties such as conductance, density and surface tension, this research work also aims the comparative study of mentioned physical parameters and micellization behavior in water and methanol-water mixed solvent media with related suitable experimental methods and materials. The main objectives of the present work are:

1. To study the critical micelle concentrations (cmc) by conductance measurement and to calculate the thermodynamic parameters like Gibbs free energy of micellization (ΔG^0_m) and the degree of micellar dissociation (α).
2. To Study the critical micelle concentration (cmc) by surface tension measurement and to calculate the surface excess concentration (Γ_{max}) and area occupied per surfactant molecule (A_{min}) of mixed surfactants.
3. To study the critical micelle concentration (cmc) by density measurement.

Chapter- 2

EXPERIMENTAL METHODS

2.1 Materials

Chemicals: In this work, sodiumdodecyl sulfate (SDS) of molecular weight 288.38 g/mol has been used manufactured from Merck Specialities Pvt. Ltd., Mumbai, India. Dodecyltrimethylammonium bromide (DTAB) of molecular weight 308.3 g/mol has been used purchased from SdFINE CHEM Ltd., Mumbai, India. Methanol (E.Merck, India, 99% pure) and triply distilled water was used for the preparations of mixed solvents in this research work.

Apparatus: The conductivity meter purchased from India was used to measure the conductivity of the different solutions. Force tensiometer K20S purchased from Germany was used for the density and surface tension measurement. Digital balance purchased from India was common in use to get exact weights of different required experimental solutions. Volumetric flasks, pipettes, pipette filler, stop watches etc were commonly used apparatus.

Washing and drying of apparatus: The glassware collected from the lab were immersed in chromic acid for about an hour and was washed thoroughly with tap water for several times with the help of brush. Then after, single distilled water was used for washing once again followed double distilled water and finally rinsing with acetone. After, washing and rinsing glassware were left for natural drying before use. These treatments were repeated as per requirement.

2.2 **Methods**

Conductometry

It is a very simple method, which allows enough precise values of the cmcs for ionic surfactants. Necessary conditions for obtaining the most accurate values are the constant temperature maintenance through the whole measuring process and the eliminations of impurities influencing the movement of charged species in the solution. It is based on the finding of a breaking point on the curves, which describes the concentration dependence of conductivity. As we know, that the conductivity of any solution is directly proportional to the concentration of its ions. It can be also used for the evaluation of the cmc data for mixed micelles systems and for the surfactants with a small aggregation number. However, conductometry provides the cmc of a mixed surfactant solution as the intersection of two straight lines in the pre and post micellar region of the specific conductivity (©) vs surfactant concentration profile.

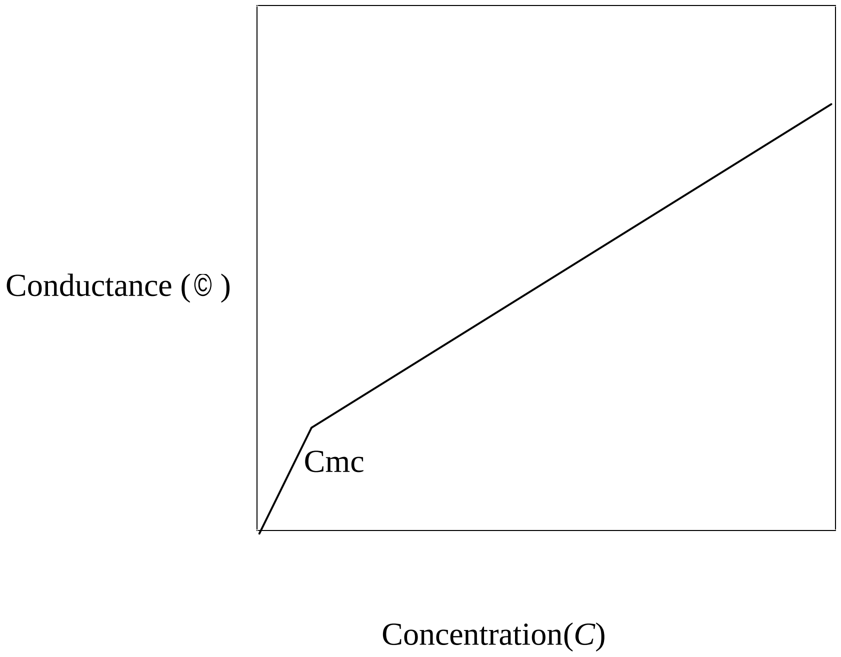


Figure 14. Specific conductivity (©) as a function of concentration

Also with the help of cmc, we can calculate important thermodynamic parameters such as Standard Gibbs free energy of micellization:

$$\Delta G_{\mathrm{m}}^{-} = RT(2-\sim)\ln X_{\mathrm{CMC}} \qquad (4)$$

where, $\sim$ = degree of dissociation

X_{CMC} = average CMC of the surfactant in mole fraction unit.

R= Universal Gas Constant

T= Temperature

Tensiometry and surface properties

The surface free energy of surface tension is the work required to increase solution molecules interact with each other, either with attractive or repul-sive forces. The molecules situated at the surface of the solution experi-ence as an imbalance in the forces where net effect represents the excess free energy at the surface. Thus, the existence of a surface tension can be expected from the difference in energy between the molecules in the bulk phase and at the surface of the solution. The surface free energy per unit area, defined as the surface tension (γ). Since, due to the surface activity of the surfactant, surface tension measurement is the major method for the determination of cmc. In this method, surface tension of a solution is measured at a number of concentrations both above and below the cmc and results plotted against the logarithm of surfactant concentration. The cmc is then taken as the "break point" or intersection of straight lines drawn through data representing the limiting surface tension above the cmc and the linear slope below the cmc [117]. The surface tension initially decreases with increasing concentration at surfactants and then reaches a plateau region, indicating that micelle are formed and the concentration of the break point corresponds to the critical micelle concentration.

Surface tension (ST) of water or air/water interfacial tension (γ) is reduced by the adsorption of surfactant at the interface, and the sigmoidal γ-log (surfactant) or logC course produces a distinct break in the plot with al-most unchanged γ thereafter, which is taken as the critical micelle concentration (cmc) of the surfactant. By surface tension measurement and applying Gibbs adsorption equation (5), the surface excess of the surfactant (Γ) relative to the water can be estimated at any (surfactant) up to the cmc, where Γ is taken as the maximum Gibbs equation for surface excess [118] is

$$\Gamma_{\max} = -\frac{1}{2.303\,nRT} \lim_{C \to CMC} \left(\frac{d¥}{d \log |C|} \right) \qquad (5)$$

where, the pre factors n is the number of species formed in solution by the dissociation of the surfactant (for a non ionic candidate, n= 1; surfactant, n= 2); and R and T have their usual significance. The $\Gamma_{\max}$ values are expressed in moles per meter square unit.

The area occupied per surfactant molecule ($A_{\min}$) at the air-water interface [119] has been obtained by using the equation below:

$$A_{\min} = 1 / N\Gamma_{\max} \qquad (6)$$

where, N = Avogadro's number

Density

Volumetric, Viscometric and thermodynamic data provide valuable information regarding solute-solvent, solute-solute and solvent-solvent interactions. Among various physical parameters, densities have been recognized are the quantities that are sensitive to structural changes occurring in solutions [120]. The density of a substance is the mass per unit volume and is represented by ρ. For the density measurement, the experiment bases on the fact that as a result of the buoyancy of a solid in a liquid the measured weight in a liquid is less than that measured in air. The mass of the volume of liquid displaced by the measuring probe corresponds to the difference in weight (Archimedes' Principle). If the density of the measuring probe is known then the density of the liquid can be obtained by differential weighing.

The equation for the calculation is:

$$^{\circ}{}_{\mathrm{L}} = {}^{\circ}{}_{\mathrm{MP}} \times G_{\mathrm{MPA}} - G_{\mathrm{MPL}} / G_{\mathrm{MPA}} \qquad (7)$$

where, $^{\circ}{}_{\mathrm{L}}$ = density of liquid; $^{\circ}{}_{\mathrm{MP}}$ = density of measuring probe;

G_{MPA}= weight of measuring probe in air; G_{MPL}= weight of the measuring probe in the liquid.

There are several methods to obtain cmc. Also very less literature regarding the calculation of cmc from density measurement was found [121-123]. In this method, it shows the variation of densities of the solution as a function of the surfactant concentration. When a density of a solution is plotted against surfactant concentration, then the intersection between two straight lines give the cmc. It is evident that the densities exhibits almost increase with increasing concentration with in concentration range.

2.3 Procedure

Preparation of the solution

Sodiumdodecyl sulfate (SDS) and Dodecyltrimethylammonium bromide (DTAB) solution preparation:

Methanol was first distilled with phosphorus pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.7772gcm^{-3} and a coefficient of viscosity of 0.4742 mPa.s at 308.15 K; these values are in good agreement with those found in the literature [124]. Triply distilled water with a specific conductance lower than 10^{-6} S.cm^{-1} at 308.15 K was used for the preparation of the mixed solvents. When methanol and water were mixed, a minute but measurable enthalpy of solution was observed. Hydrogen bonding and the close hydrated methanol molecules to fit into the same space, thus decreasing the overall volume. The volume of the solution containing a 0.40 volume fraction of methanol decreased more than that of the solution containing a 0.30, 0.20 and 0.10 volume fraction of methanol: therefore, the higher the amount of methanol, the more the decreases in volume in the volumetric flask. Moreover, the density decreased with the increase in alcohol content for the methanol water mixed solvent media [125].

Dodecyltrimethylammonium bromide (DTAB) was recrystallized several times until no minimum in the surface tension-concentration plot was observed and its critical micellar concentration (cmc) agreed with the literature value [71].

Sodiumdodecyl sulfate was recrystallized several times for purification. A minimum in the surface tension concentration plot was observed. The aqueous solution of the purified and unpurified samples of sodiumdodecyl sulfate exhibited a minimum in the surface tension versus logC plot (where c is the concentration of sodiumdodecyl sulfate). The minimum in the γ versus logC plot for sodiumdodecyl sulfate is considered to be due to the presence of highly surface active dodecyl alcohol molecules [31]. Dodecyl alcohol may be present as an impurity in the supplied sample of sodiumdodecyl sulfate or may be produced in the sodiumdodecyl sulfate solution by hydrolysis. The cmc of SDS is taken to be the concentration of sodiumdodecyl sulfate corresponding to the minimum in the γ versus logC plot and is equal to 8.10mmol.kg^{-1} in the absence of any added electrolyte at 25^{0}C. This value is in good agreement with cmc of sodiumdodecyl sulfate obtained from conductance measurement (8.10mmol.kg^{-1}) [126].

Triply distilled water and 0.10 to 0.40 volume fraction of methanol were used to make~9.0×10^{-4} mol.lt^{-1} solution of dodecyltrimethylammonium bromide. The solutions of dodecyltrimethylammonium bromide were further used as solvents to make~0.03×10^{-1}mol.lt^{-1} solution of sodium-dodecyl sulfate at room temperature for SDS (anionic) rich solution. Similarly for the preparation of DTAB (cationic) rich solution, triply distilled water and 0.10 to 0.40 volume fraction of methanol were used to make~9.0×10^{-4} mol.lt^{-1} solution of sodiumdodecyl sulfate. The solutions of SDS were further used as solvent to make~0.03×10^{-1}mol.lt^{-1} solution of dodecyltrimethylammonium bromide at room temperature. Both the anionic and cationic rich solutions were also prepared in pure methanol.

Conductance Measurement

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip- type cell with a cell constant of 1.15 cm^{-1} and having an uncertainity of 0.01%. The cell was calibrated using aqueous potassium chloride solution [127].

For the conductance measurement of SDS (anionic) rich solution in distilled water, conductivity cell was rinsed several times with distilled water and acetone and were left for natural drying. Then after a suitable SDS rich solution in distilled water was selected with a concentration of 0.04M (S_1). A clean and dry graduated glass beaker of 50ml was taken and was filled with about 40ml of that solution (S_1). After that, corresponding conductance shown by conductivity meter was noted down. Then 5ml of the test dilution of first surfactant solution i.e. internal dilution and second conductance value was taken. The conductance cell contents were stirred after each addition at room temperature. And several readings were taken until same approximate readings were obtained. The wide range of concentration of S_1 obtained by internal dilution method, were estimated with Microsoft excel program and corresponding conductance were noted and tabulated. Now, the tabulated concentrations and specific conductance were plotted by easy plot software and most importantly, at the last cmc value was calculated. Similarly, to measure the conductance of SDS rich solution of different concentration, essential procedures were followed as mentioned earlier for distilled water.

Also, for the conductance measurement of DTAB (cationic) rich solution in distilled water, conductivity cell was rinsed several times with distilled water and then with acetone and were left for natural drying. After that a suitable DTAB rich solution in distilled water was selected with concentration of 0.03M (S_2). Similar procedures were followed as mentioned above for anionic (SDS) rich solution of different concentration and lastly the cmc values were calculated.

Surface Tension Measurement

In this method, for both anionic (SDS) rich solution and cationic (DTAB) rich solution, surface tension measurements were determined with a Kruss K20S force tensiometer, Germany using a platinum ring by the ring detachment technique at a room temperature. The tensiometer was calibrated against distilled water. The tensiometer was calibrated against distilled water. The platinum ring was thoroughly cleaned with distilled water and acetone and left for natural dry before each measurement. To measure the surface tension, the vertically hung ring was dipped into the solution and then pulled out. Prior to detachment, the platinum-iridium ring was carefully lifted. The maximum force required to pull the ring through the interface is then the surface tension: γ (mN/m). Similar processes were carried out for the solution of different concentration. Each sample solution was stirred with a magnetic stirrer and then the stirring of the sample was discontinued for 3 minutes and the surface tension was measured. Each experiment was repeated several times until good reproducibility was achieved. Several reading were noted and tabulated. The tabulated surface tension (γ) and logC (i.e. C is the surfactant concentration plotted and the cmc values were calculated.

Density Measurement

For the measurement of density in cases of both SDS (anionic) rich solution and DTAB (cationic) rich solution, were performed using a Kruss K20S force tensiometer at a room temperature. The tensiometer was calibrated against distilled water, the holder for the density probe and the probe itself was thoroughly cleaned with distilled water, acetone and kept for a while to natural dry before each measurement. To measure the density, holder was hung vertically; the clean density body (i.e. probe) was attached to the holder and waited until the holder along with the density body no longer moved. The weight of the density body was determined in air, immediately after that the density body was removed from the holder. Again, the vertically hung holder was dipped into the solution up to the yoke and pressed tare to tare the weight of the holder in the liquid. The sample stage was moved downward and the weight to the holder was attached with the help of tweezers. Now, the holder with the density body was dipped in the solution to exactly the same depth as during the taring process and waited until the holder with density body no longer moved and the liquid had come to rest. Finally, the density of the solution was measured and noted. For every measurement, sample solution was stirred with a magnetic stirrer and then the stirring of the sample was discontinued for 3 minutes.

Similar procedures were followed for the measurement of densities of solutions having different concentration and several readings were taken. The tabulated density (ρ) and concentrations were plotted and at the last cmc values were calculated.

RESULTS AND DISCUSSION

3.1. Conductance Measurement

The conductance of sodiumdodecyl sulfate in the presence of dodecyltrimethylammonium bromide in pure water and in three different methanol-water mixtures (containing 0.10, 0.20, and 0.30 volume fractions of methanol) and its vice-versa for the calculation of the critical micelle concentration at room temperature are depicted in Figures 15-18, whereas the measured conductances are reported in Appendix. For anionic rich (SDS in the presence of DTAB) solution containing 0.40 volume fraction of methanol, a sharp break in cmc was not seen, while in case of cationic rich (DTAB in the presence of SDS) solution containing 0.40 volume fraction of methanol, the prepared solution appeared cloudy. Similarly, anionic rich solution appeared cloudy in pure methanol where as for cationic rich solution; conductance values noted were almost linear.

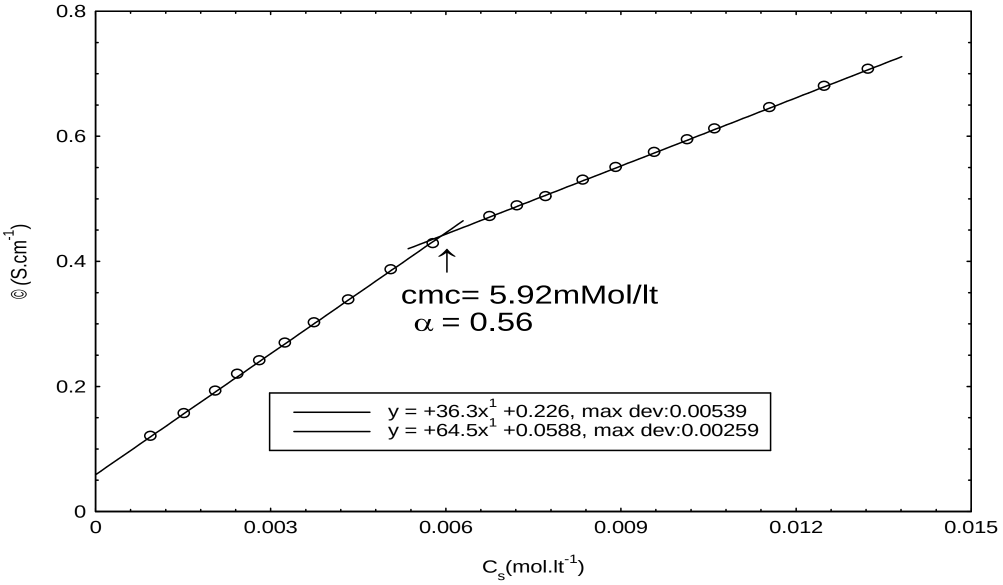


Figure 15A. Concentration dependence of the conductance for sodiumdodecyl sulfate in the presence of dodecyltrimethylammonium bromide in pure water at room temperature: the intersection between two straight lines gives the critical micelle concentration (cmc)

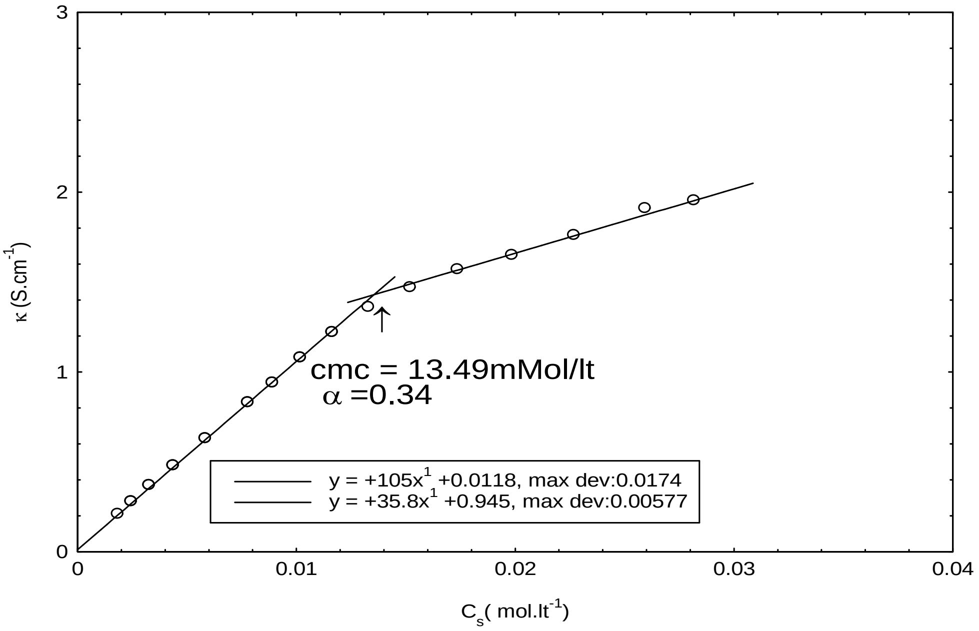


Figure 15B. Concentration dependence of the conductance for dodecyltrimethylammonium bromide in the presence of sodiumdodecyl sulfate in pure water at room temperature: the intersection between two straight lines gives the critical micelle concentration (cmc)

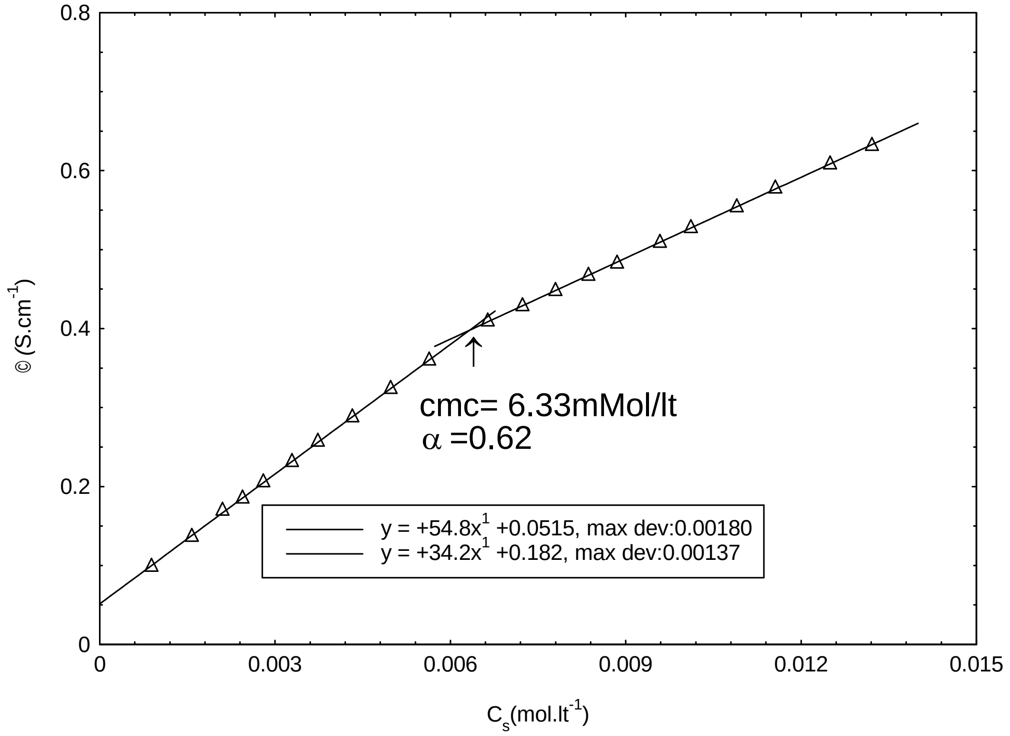
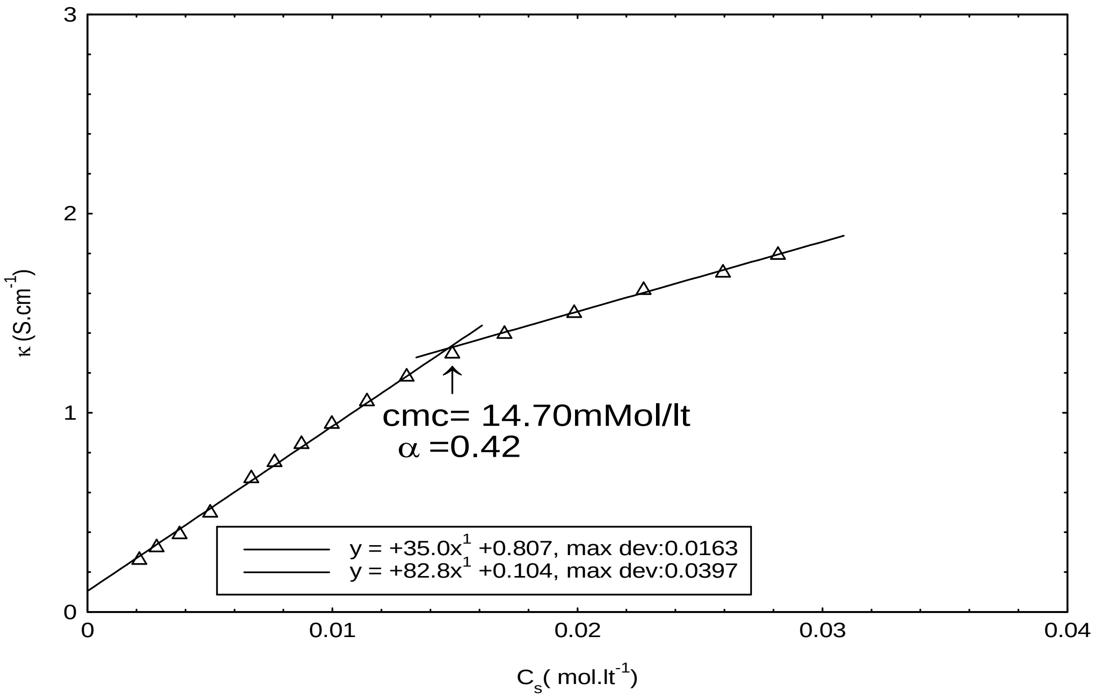


Figure 16A. Concentration dependence of the conductance for sodiumdodecyl sulfate in the presence of dodecyltrimethylammonium bromide in 0.10 methanol at room temperature: the intersection between two straight lines gives the critical micelle concentration (cmc)



Fig

Figure 16B. Concentration dependence of the conductance for dodecyltrimethylammonium bromide in the presence of sodiumdodecyl sulfate in 0.10 methanol at room temperature: the intersection between two straight lines gives the critical micelle concentration (cmc)

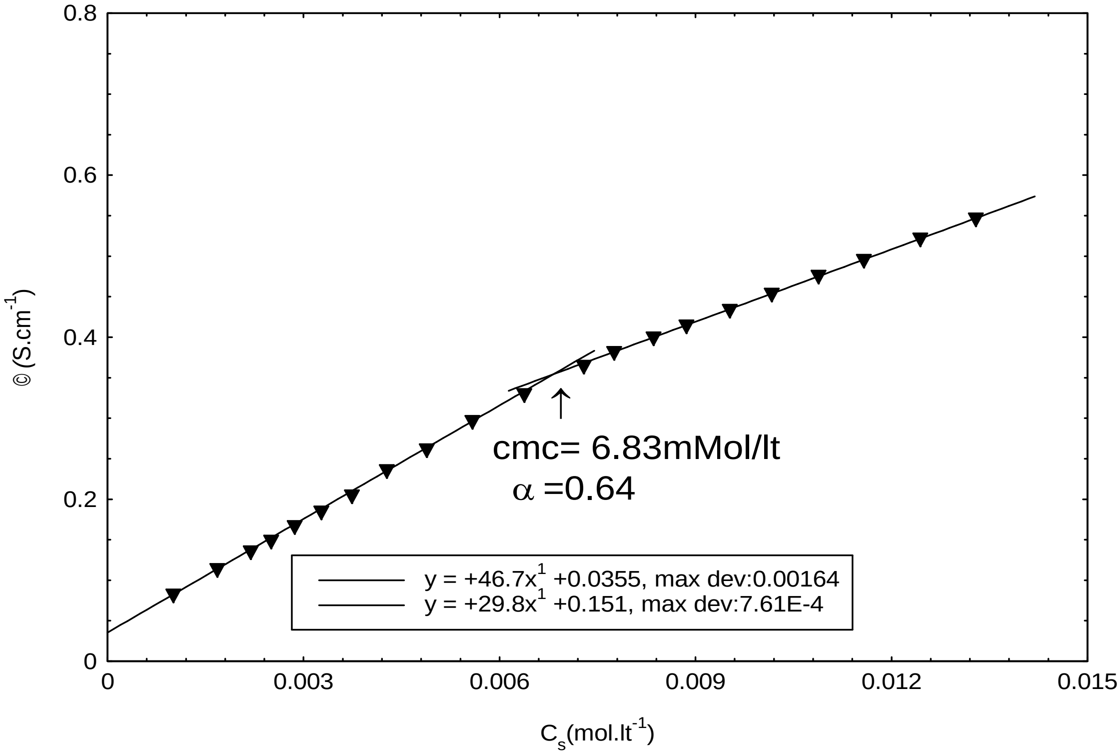


Figure 17A. Concentration dependence of the conductance for sodiumdodecyl sulfate in the presence of dodecyltrimethylammonium bromide in 0.20 methanol at room temperature: the intersection between two straight lines gives the critical micelle concentration (cmc)

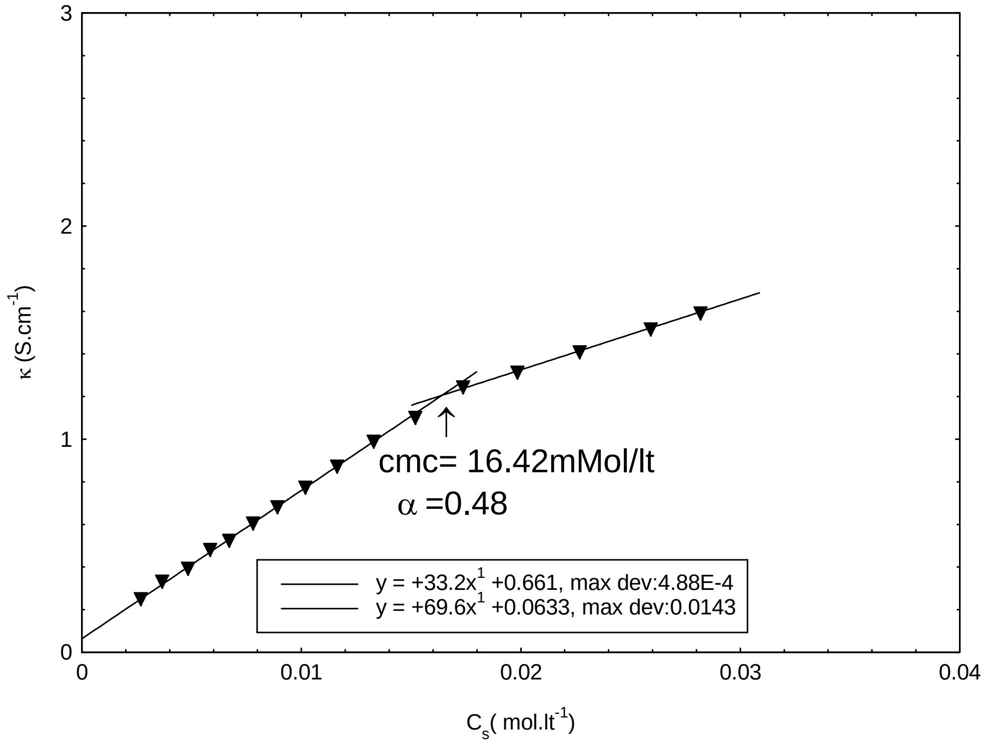


Figure 17B. Concentration dependence of the conductance for dodecyltrimethyl-ammonium bromide in the presence of sodiumdodecyl sulfate in 0.20 methanol at room temperature: the intersection between two straight lines gives the critical micelle concentration (cmc)

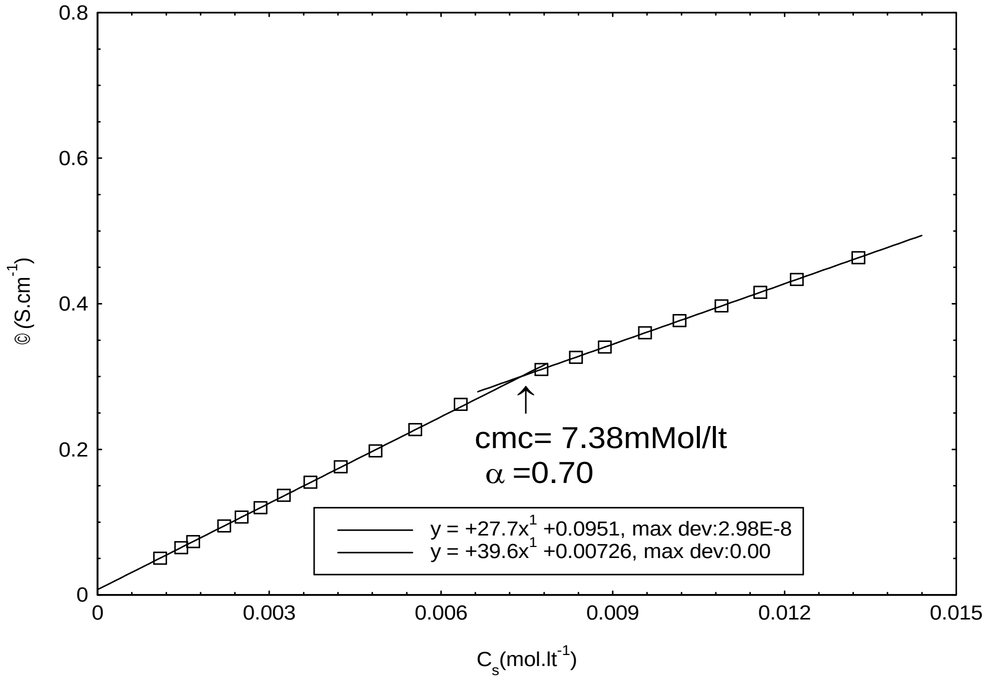


Figure 18A. Concentration dependence of the conductance for sodiumdodecyl-sulfate in the presence of dodecyltrimethylammonium bromide in 0.30 methanol at room temperature: the intersection between two straight lines gives the critical micelle concentration (cmc)

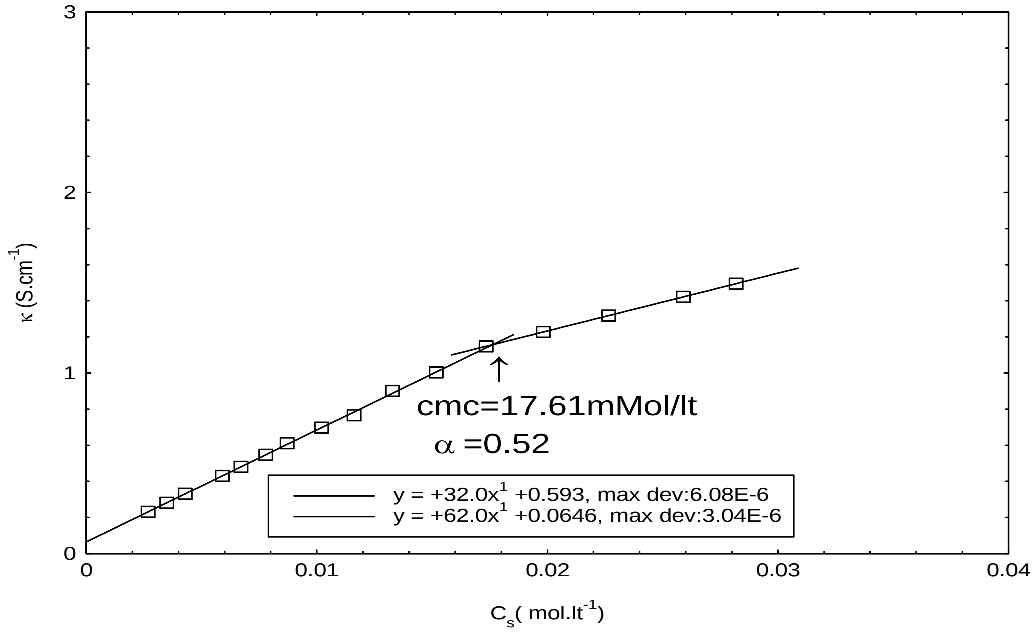


Figure 18B. Concentration dependence of the conductance for dodecyltrimethylammonium bromide in the presence of sodiumdodecyl sulfate in 0.30 methanol at room temperature: the intersection between two straight lines gives the critical micelle concentration (cmc)

Figures 15-18 show the variation of the conductance of the investigated solutions as a function of the anionic rich i.e. SDS in the presence of DTAB and as a function of cationic rich i.e. DTAB in the presence of SDS concentration in the surfactant mixtures. From these Figures, it is evident that the conductance exhibits a sharp increase for both cases with increasing SDS and DTAB concentration within the concentration range investigated here. The increase in conductance with concentration is due to an increase in the number of ions per unit volume of the solution. The rise in conductance with temperature is due to the decrease in the viscosity of the solution, increase in the speed of the ions and increase in the degree of ionization.

From representative figure 19, the conductance of sodiumdodecyl sulfate in the presence of dodecyltrimethylammonium bromide and dodecyltrimethyl ammonium bromide in the presence of sodiumdodecyl sulfate at room temperature in pure water and in three different methanol-water mixtures (containing 0.10, 0.20 and 0.30 volume fractions of methanol), it is observed that the conductance decreases with the increase in alcohol content in the mixed solvent systems. The presence of methanol reduces the dielectric constant of the solvent phase and makes the formation of ion pairs in the solution phase easier. In other words, in solvents of low dielectric constants, which have a small ionizing effect on surfactants, the electrostatic forces between oppositely charged ions account for the small value of the conductance. Conversely, solvents with high dielectric constants yield more conducting solutions.

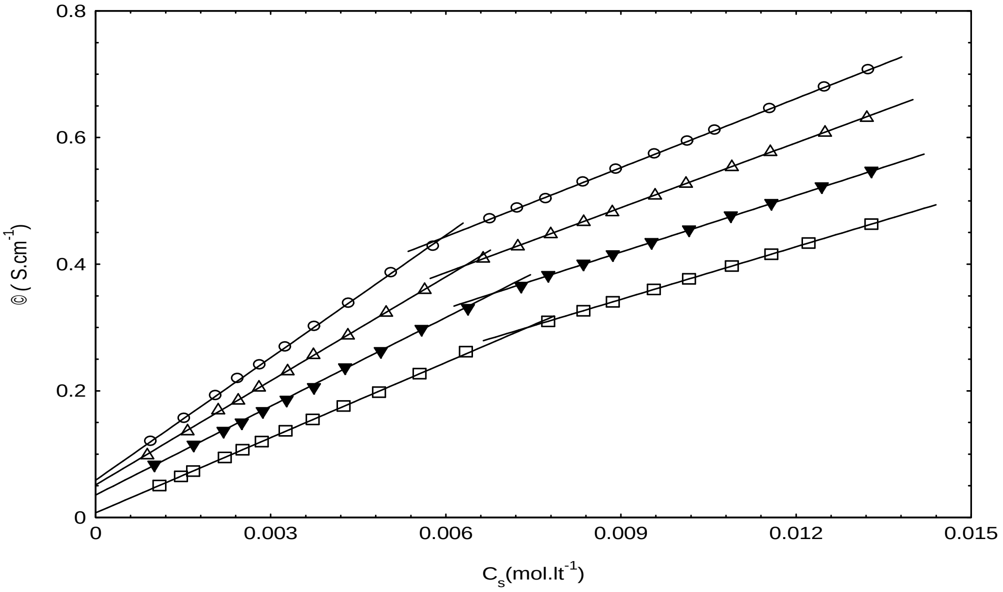


Figure 19A. Concentration dependence of the conductance for sodiumdodecyl sulfate (SDS) in the presence of dodecyltrimethylammonium bromide (DTAB) at room temperature, in pure water (open circle) and different methanol-water mixtures (triangles, 0.10 volume fraction of methanol; closed inverted triangles, 0.20 volume fraction of methanol; squares, 0.30 volume fraction of methanol)

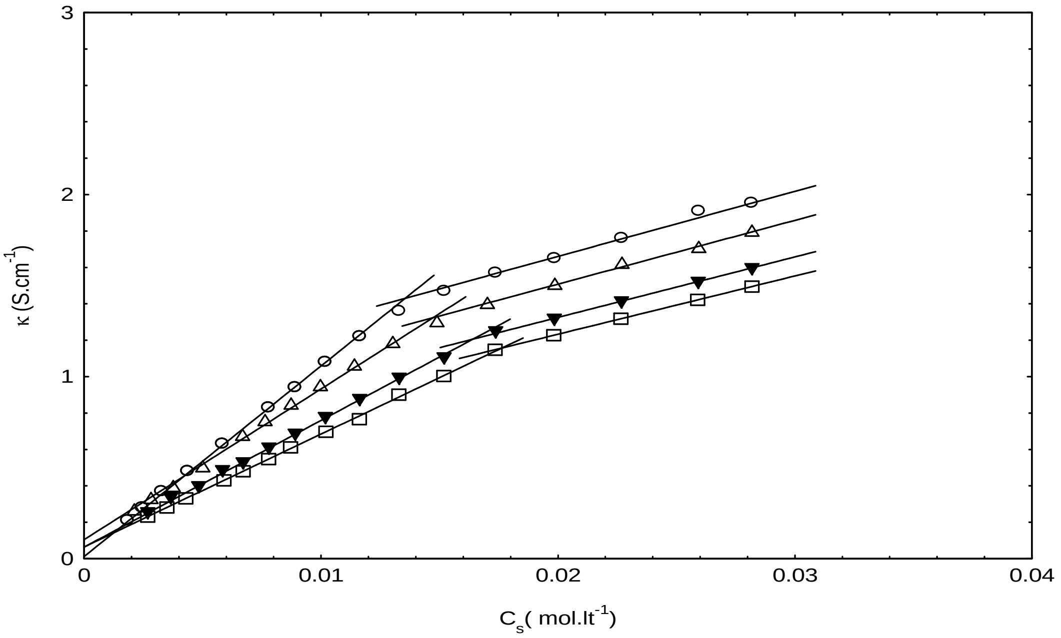


Figure 19B. Concentration dependence of the conductance for dodecyltrimethyl-ammonium bromide in the presence of sodiumdodecyl sulfate at room tempera-ture, in pure water (open circle) and different methanol-water mixtures (open triangles, 0.10 volume fraction of methanol; closed inverted triangles, 0.20 volume fraction of methanol; squares, 0.30 volume fraction of methanol)

For critical micelle concentration calculations, the specific conductivity, © of the mixed surfactant solutions is plotted against the concentration. The break in the curves, corresponding to micelle formation and observed at specific concentration, is called the critical micelle concentration (cmc).

The variation of the specific conductivity values before and after the cmc is different. After the cmc, the conductivity decreases due to the formation of micelles having less ionic mobility.

If the specific conductivity ($\lambda = \kappa/c$) is substituted for the molar conductivity, then the specific conductivity can be plotted versus the concentration. The cmc may be determined by solving the simultaneous set of the two equations of the straight lines, as in the representative Figure 20. The slopes of the two lines in the conductivity versus surfactant concentration plot are used to calculate the degree of dissociation.

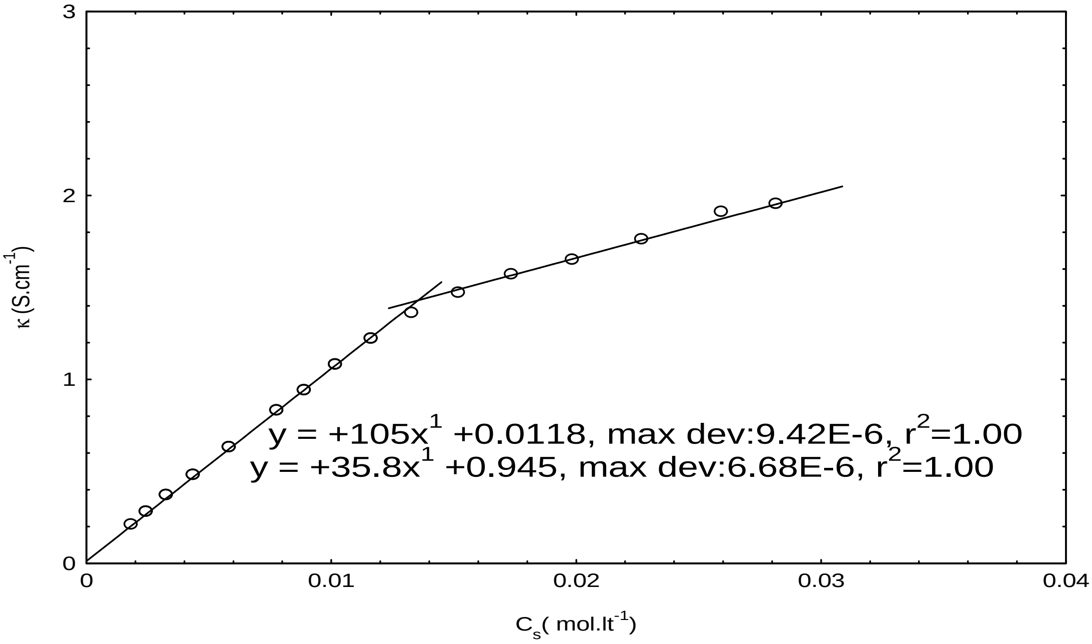


Figure 20A. Concentration dependence of the conductance for sodiumdodecyl sulfate in the presence of dodecyltrimethylammonium bromide in pure water at room temperature: linear equations with slope, intercept, maximum deviation, and correlation coefficient for critical micelle concentration (cmc) calculation

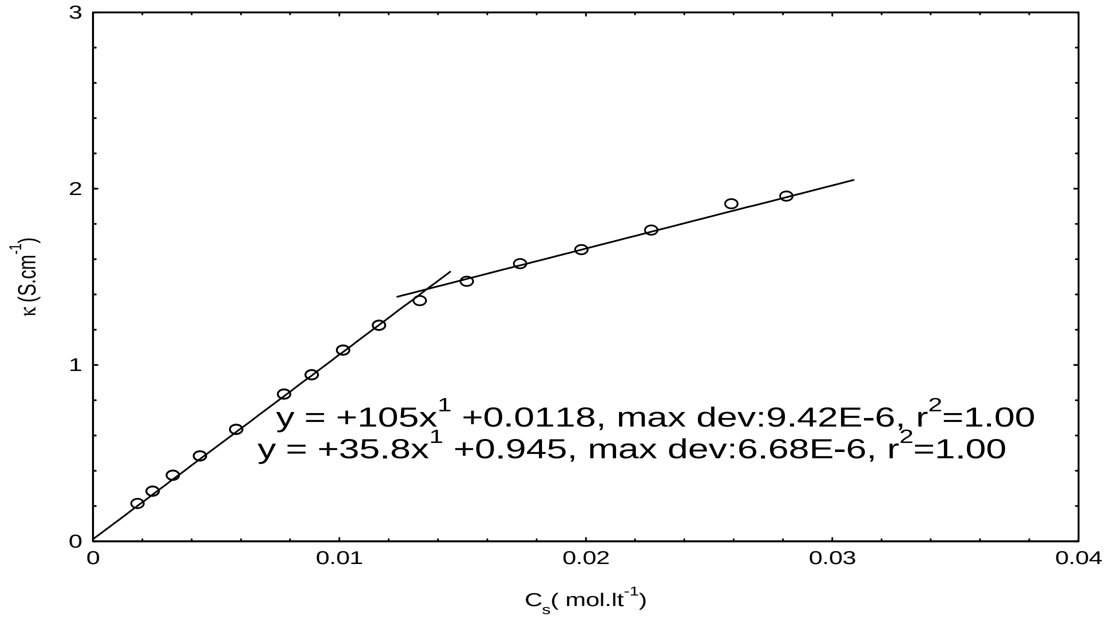


Figure 20B. Concentration dependence of the conductance for dodecyltrimethyl-ammonium bromide in the presence of sodiumdodecyl sulfate in pure water at room temperature: linear equations with slope, intercept, maximum deviation, and correlation coefficient for critical micelle concentration (cmc) calculation

The cmc is determined for both the SDS-DTAB and DTAB-SDS solutions in pure water and in the methanol-water mixed solvent media. The degree of dissociation (α) is obtained from the ratio of the slopes above and below the cmc in the conductivity versus surfactant concentration plot and is given by:

$$\alpha = S_2/S_1 \qquad (8)$$

where, S_1 is the pre-cmc slope and S_2 is the post-cmc slope[128]. The mixed surfactants show the largest pre-cmc slopes and smallest post-cmc slopes, leading to the smallest degrees of dissociation (Tables 1 and 2). Both slopes (pre-cmc and post-cmc) decrease with the increase in methanol in the methanol-water mixed solvent media. The decrease in the value of the pre-cmc slopes of the mixed surfactants is sharp in comparison with the value of the post-cmc slopes upon addition of larger volumes of methanol at room temperature (Figure 21).

Table 1. The pre-cmc slope (S_1) and post-cmc slope (S_2) for both the anionic-rich (SDS-DTAB) and cationic-rich (DTAB-SDS) system obtained from conductance measurements in pure water and in methanol-water mixed solvent media containing 0.10, 0.20 and 0.30 volume fractions of methanol at room temperature

	Anionic rich (SDS-DTAB)	Cationic rich (DTAB-SDS)
Vol. fraction of Methanol	S_1, S_2 (S/cm*mM)	S_1, S_2 (S/cm*mM)
0	64.5, 36.3	105.0, 35.8
0.10	54.8, 34.2	82.8, 35.0
0.20	46.7, 29.8	69.6, 33.2
0.30	39.6, 27.7	62.0, 32.0

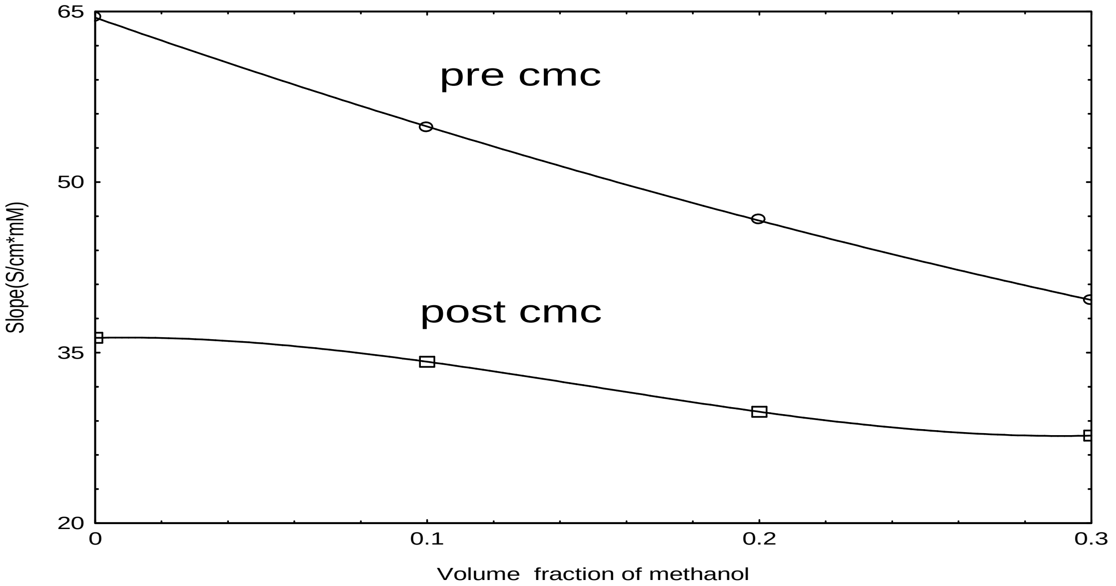


Figure 21A. Variation of the slope with the volume fraction of methanol in methanol-water mixed solvents for the conductivity of SDS-DTAB solutions at room temperature

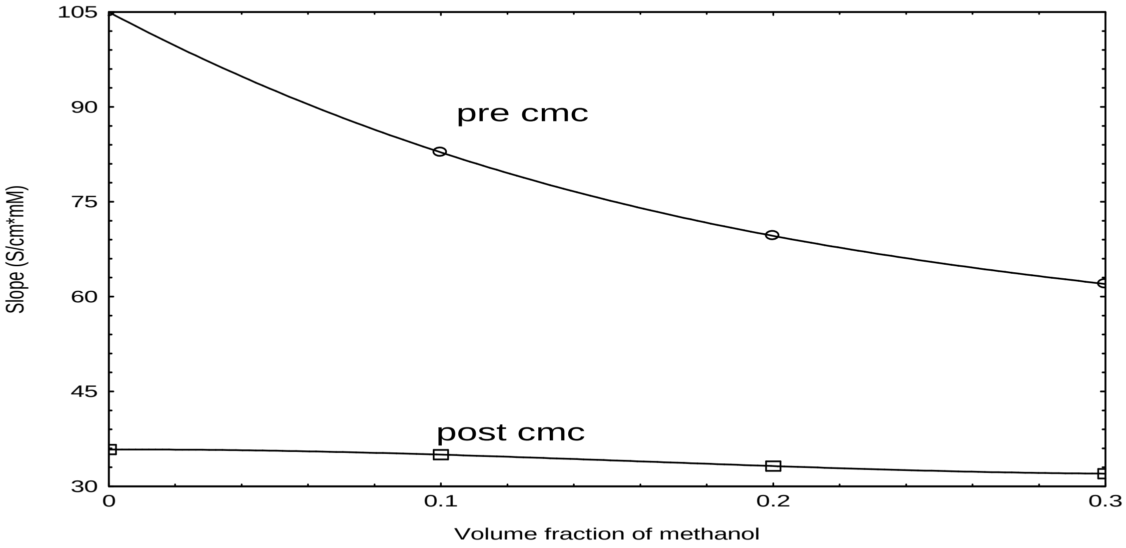


Figure 21B. Variation of the slope with the volume fraction of methanol in methanol-water mixed solvents for the conductivity of DTAB-SDS solutions at room temperature

The critical micelle concentration (cmc) obtained for both the SDS-DTAB and DTAB-SDS system from conductometry measurements in pure water and in methanol-water mixed solvent media containing 0.10, 0.20, and 0.30 volume fractions of methanol at room temperature is shown in Table 2.

It is observed that both the cmc and α increase with the increase in methanol in the methanol-water mixed solvent medium (Table 2).

Table 2. The critical micelle concentration (cmc) and degree of dissociation (α) obtained for the anionic-rich (SDS-DTAB) and cationic-rich (DTAB-SDS) systems from conductometry measurements in pure water and in methanol-water mixed solvent media containing 0.10, 0.20, and 0.30 volume fractions of methanol at room temperature

	Anionic rich (SDS-DTAB)	Cationic rich (DTAB-SDS)
Vol. fraction of methanol	cmc[mmol.l^{-1}], α	cmc[mmol.l^{-1}], α
0	5.92, 0.56	13.49, 0.34
0.10	6.33, 0.62	14.70, 0.42
0.20	6.83, 0.64	16.42, 0.48
0.30	7.38, 0.70	17.61, 0.52

In this work, a higher concentration of anionic surfactant (SDS) was used because it interacts with cationic surfactant hydrophobically and favors micellization as anionic surfactants are known for having stronger hydrophobic interactions compared with cationic surfactants [129, 130]. The ratios of sodiumdodecyl sulfate (SDS) to dodecyltrimethylammonium bromide (DTAB) as well as DTAB to SDS were 1:3. Therefore, the cmc of sodiumdodecyl sulfate (SDS) in the presence of dodecyltrimethylammonium bromide (DTAB) decreased to a value of 5.92 mM in comparison with the cmc of 8.0 mM of sodiumdodecyl sulfate [131] (SDS) and cmc of dodecyltrimethylammonium bromide (DTAB) in the presence of sodiumdodecyl sulfate (SDS) decreased to a value of 13.49 mM in comparision with the cmc of 14.5 mM of dodecyltrimethylammonium bromide (DTAB) [71] at room temperature. The decrease in cmc is due to the larger synergistic effects when two oppositely charged surfactants are mixed together. A similar behavior was noticed by Herrington and Kaler [58] in 1993 when they studied the phase behavior of aqueous mixtures of dodecyltrimethylammonium bromide (DTAB) and sodiumdodecyl sulphate (SDS) and found a decrease in cmc and conductivity of SDS-rich aqueous solutions for various mixing ratios of DTAB to SDS as a function of total surfactant concentration and vice-versa. Hence the cmc obtained for the investigated system in the present work is consistent with literature values.

The change in cmc with increasing concentrations of methanol at room temperature is shown in Figure 22. As alcohol is added to a surfactant mixture solution, the dielectric constant and degree of structuring of the solvent are lowered. As more alcohol is added, this process continues and the micelles expand, hence leading to an increased cmc. Similar trends have been observed [132] who concluded that there is a significant increase in the cmc of surfactants with the increase in the volume fraction of ethanol. It is clear from Table 2 and Figure 22 that on increasing the volume fraction of methanol, the cmc also increases.

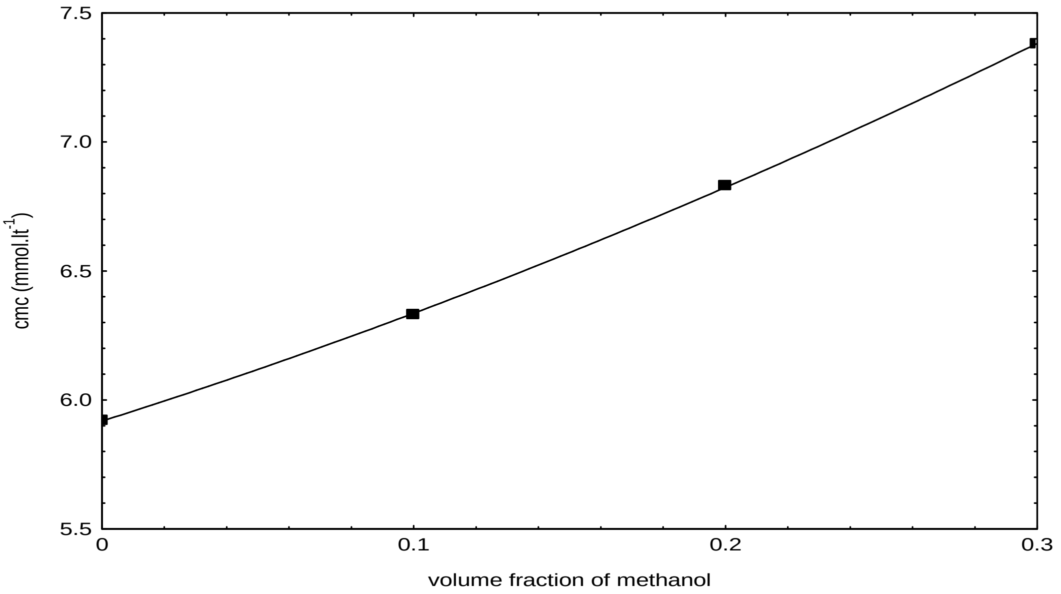


Figure 22A. Variation of the cmc of SDS in the presence of the DTAB solution as a function of the volume fraction of methanol at room temperature

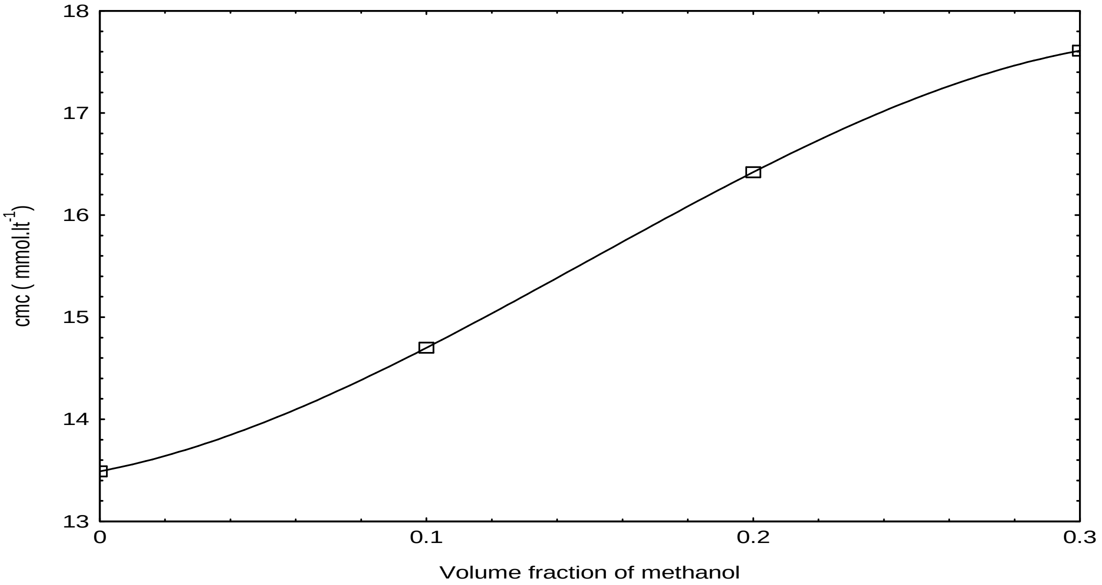


Figure 22B. Variation of the cmc of DTAB in the presence of the SDS solution as a function of the volume fraction of methanol at room temperature

The degree of dissociation (*α*) obtained for the anionic-rich (SDS-DTAB) and cationic-rich (DTAB-SDS) system from conductometry measurements in pure water and in methanol-water mixed solvent media containing 0.10, 0.20, and 0.30 volume fractions of methanol at room temperature is given in Table 2.

It is known that an increase in the organic solvent content decreases the aggregation number of the micelles, which then causes an increment in the electrostatic repulsion between the cationic head group of DTAB and the anionic surfactant, i.e. SDS, and leads to a diminution in the electrical charge density at the micellar surface. This may be the reason for the increase in *α* [133,134].

The free energies of micelle formation are calculated using the following equation [135]:

$$\Delta G^{-}_{\mathrm{m}} = RT(2-\sim)\ln_{\mathrm{CMC}} \qquad (9)$$

where, R and T have their usual meaning. Here in equation (9) CMC is expressed in mol/lt in the past literature [136] but according to the recent literature [118], the scale in mole fraction is unitary. In the unitary scale one can compare different solvents (pure or mixed) at comparable compositions or moles. In molar solution of water and alcohol, the total volume is one liter but one liter of water and one liter of alcohol do not have equal moles (water has more molecules than that of alcohol). But in 0.5 mole fraction, both mixtures have equal number of solute and solvent. This is true in all compositions. Thus, the mole fraction scale is a better choice. In that scale also the contribution of the solvent molecules on the process of thermodynamics is taken care of, so eq^{n} (9) can written as ;

$$\Delta G^{-}_{\mathrm{m}} = RT(2-\sim)\ln X_{\mathrm{CMC}} \qquad (10)$$

It is evident from Table 3 that the free energy of micelle formation is negative in all cases and becomes less negative as the methanol content in the mixed solvent system increases, indicating that the formation of micelles becomes less spontaneous at higher methanol content. This behavior suggests that aggregation becomes less favorable at higher methanol contents. Similar trends were also observed by Moya et al. [71] and several other research groups [86, 137-141].

Table 3. Thermodynamic parameters of the micellization of anionic-rich (SDS-DTAB) and cationic-rich (DTAB-SDS) solutions in pure water and methanol-water mixed solvent media.

Volume fraction of methanol	ΔG_m^{-} (kJ/mol)(anionic rich)	ΔG_m^{-} (kJ/mol)(cationic rich)
Pure water	-31.87	-33.95
0.10 volume fraction of methanol	-30.34	-31.81
0.20 volume fraction of methanol	-29.25	-29.96
0.30 volume fraction of methanol	-27.60	-28.68

3.2. Surface Tension Measurement

The surface tension values of sodiumdodecyl sulfate (SDS) in the presence of dodecyltrimethylammonium bromide (DTAB) and its vice-versa in pure water and in three different methanol water mixtures (containing 0.10, 0.2 0, and 0.30 volume fraction of methanol) were plotted against logarithm of concentration for the calculation of critical micelle concentration at room temperature are illustrated in Figures 23-24, whereas the measured surface tension values are reported in Appendix.

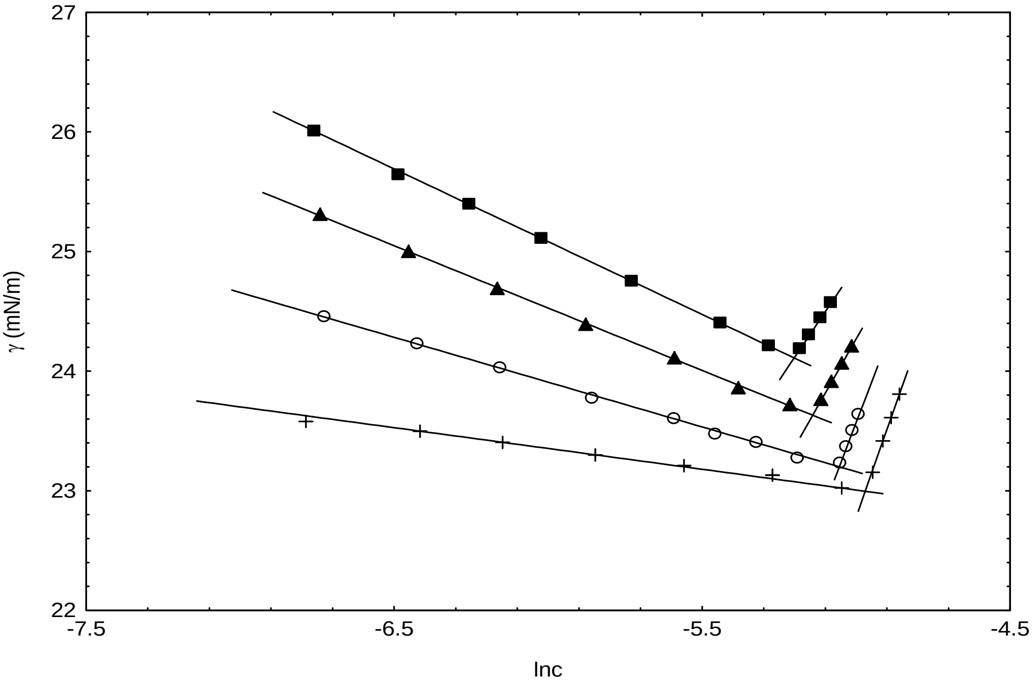


Figure 23A. Plot of surface tension versus lnC for anionic-rich mixtures (SDS in the presence of DTAB) at room temperature, in pure water (closed squares) and different methanol-water mixtures (closed triangles, 0.10 volume fraction of methanol; open circles, 0.20 volume fraction of methanol; crosses, 0.30 volume fraction of methanol)

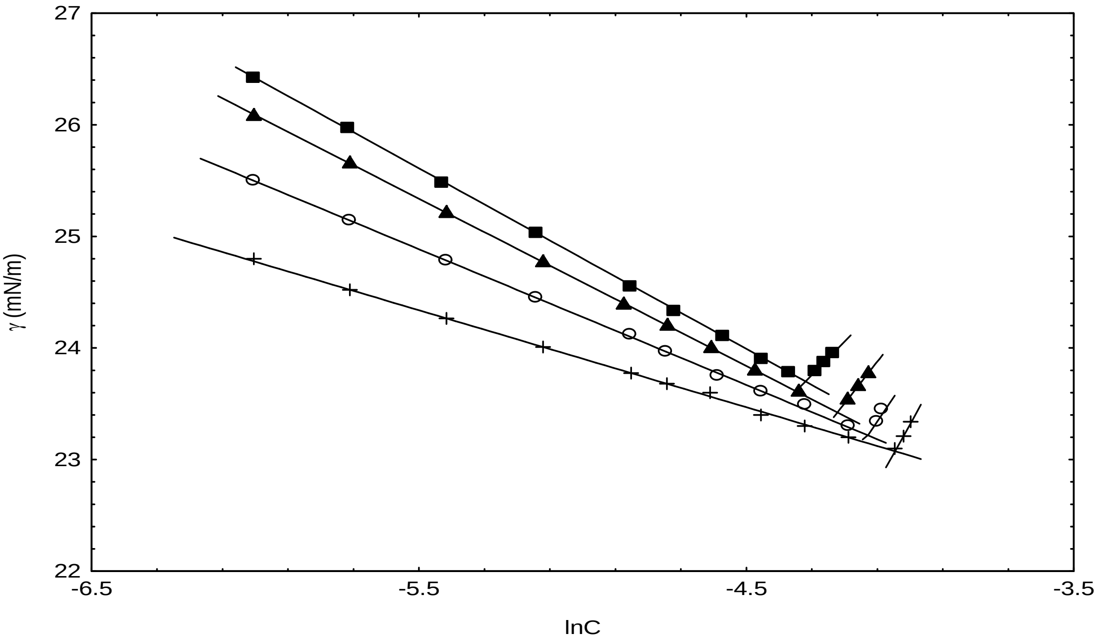


Figure 23B. Plot of surface tension versus lnC for cationic-rich mixtures (DTAB in the presence of SDS) at room temperature, in pure water (closed squares) and different methanol-water mixtures (closed triangles, 0.10 volume fraction of methanol; open circles, 0.20 volume fraction of methanol; crosses, 0.30 volume fraction of methanol)

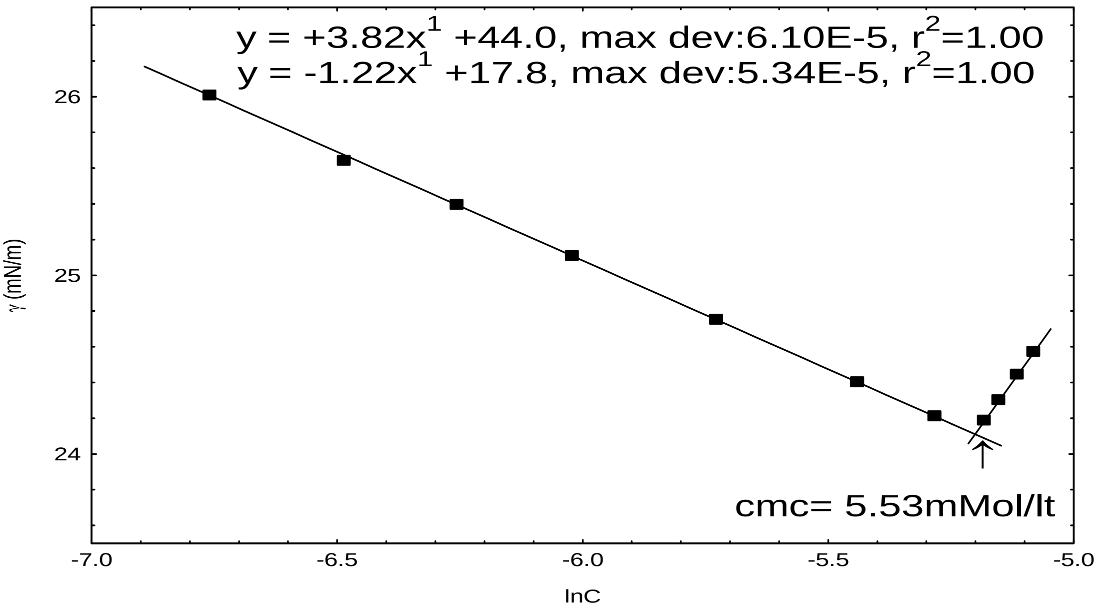


Figure 24A. Plot of surface tension versus lnC in pure water for anionic-rich surfactant mixture (SDS in the presence of DTAB) room temperature: linear equations with slope, intercept, maximum deviation, and correlation coefficient for critical micelle concentration (cmc) calculation

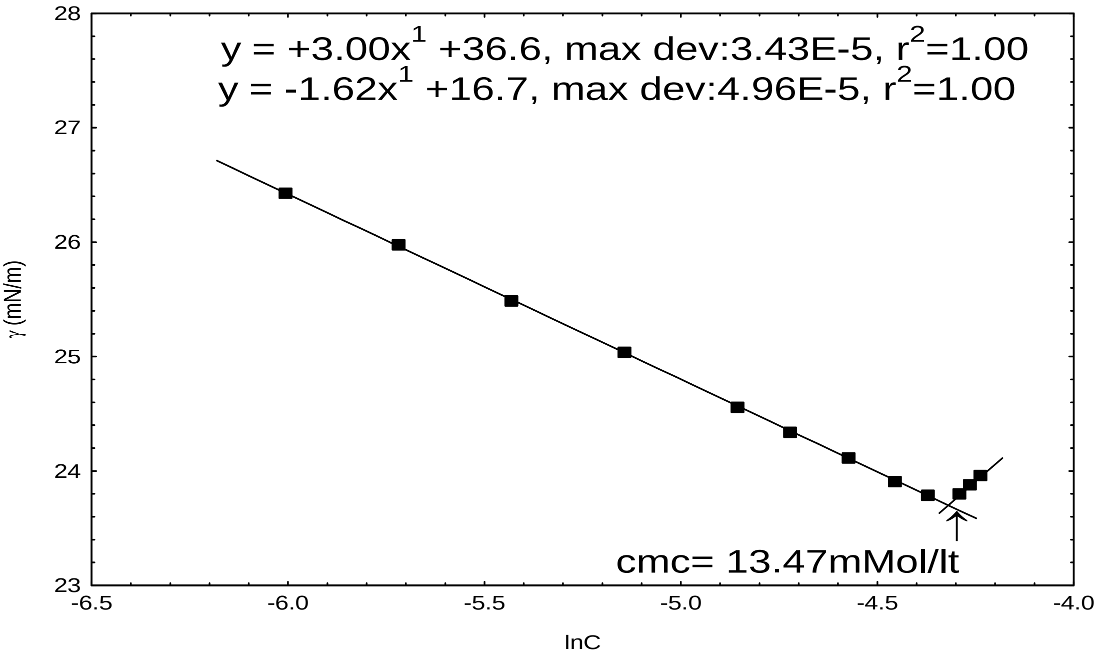


Figure 24B. Plot of surface tension versus lnC in pure water for cationic-rich surfactant mixture (DTAB in the presence of SDS) room temperature: linear equations with slope, intercept, maximum deviation, and correlation coefficient for critical micelle concentration (cmc) calculation

From above Figure (23), it is evident that the surface tension initially decreases with increasing concentration of surfactants for both cases anionic-rich i.e. SDS in the presence of DTAB and cationic-rich i.e. DTAB in the presence of SDS, and then reaches a plateau region, indicating that micelle are formed and the concentration of the breakpoint corresponds to the critical micelle concentration (cmc).

For critical micelle concentration calculations, the surface tension (γ) of the mixed surfactant solution is plotted against lnC (i.e. C is the surfactant concentration) as shown in the Figure (24). Variation of slope, $\frac{d\gamma}{d\log C}$ with volume fraction of methanol strongly affect the surface properties of surfactant solution as the slope is the key factor for the calculation of surface properties is illustrated in figure below:

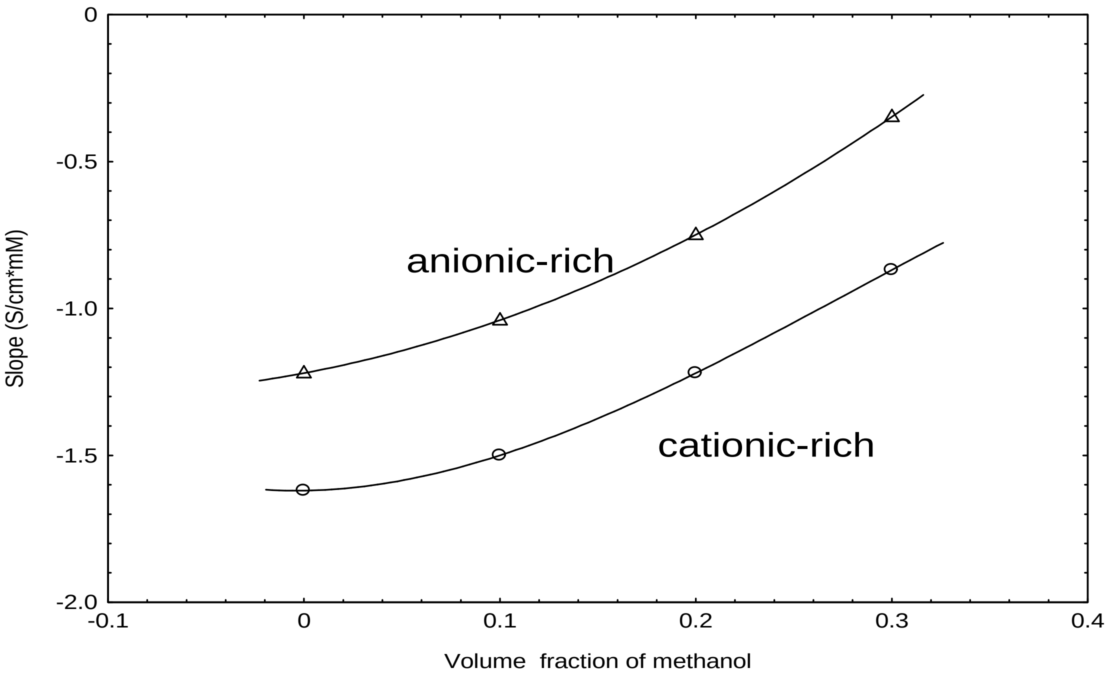


Figure 25. Variation of the slope with the volume fraction of methanol in methanol-water mixed solvents for the surface tension measurement of anionic rich (SDS-DTAB) and cationic rich (DTAB-SDS) solutions at room temperature

An increase in the volume percent of alcohol in the solution results in an increase in the cmc. The addition of alcohol affects the interaction between the hydro-phobic groups and that between the hydrophilic groups of the surfactants. Since, the dielectric constant of methanol is much lower than that of water. Thus, the addition of methanol to water will lower the dielectric constant of the mixed solvent.

The hydrophobic effect of catanionic surfactant molecules is weaker, which is a disadvantage for micelle formation. Methanol addition, on the other hand, streng-thens the attractive electrostatic interaction between their two oppositely charged polar groups and consequently is an advantage for micelle formation[142-144]. In surfactant mixtures, it overcomes the disadvantageous influence of methanol addition on the hydrophobic effect. It can be seen that the presence of methanol in the bulk phase affects the micellization process of surfactant mixtures and leads to a more spontaneous process. While in pure systems, an increase in the volume fraction of methanol causes the micellization process to occur less spontaneously. It can be understood as the basis of a reduction in the solvophobic interactions caused by the improved salvation, which leads to an increase in the solubility of the hydrocarbon tails and electrostatic repulsion between head group in the presence of methanol and consequently in an increase in the cmc as shown in the table below:

Table 4. The slope and critical micelle concentration (cmc) for both the SDS-DTAB and DTAB-SDS system obtained from surface tension measurements in pure water and in methanol-water mixed solvent media containing 0.10, 0.20, and 0.30 volume fractions of methanol at room temperature

	Anionic rich		Cationic rich	
Vol. fraction of methanol	slope (S/cm*mM)	cmc (mmol.lt^{-1})	slope (S/cm*mM)	cmc (mmol.lt^{-1})
0	-1.22	5.53	-1.62	13.47
0.1	-1.04	5.83	-1.50	14.73
0.2	-0.749	6.34	-1.22	16.25
0.3	-0.348	6.95	-0.869	17.54

The maximum surface excess concentrations of anionic-rich and cationic-rich surfactants, Γ_{max} (SDS in the presence of DTAB) and Γ_{max} (DTAB in the presence of SDS), respectively, were obtained using the surface tension measurement and has been calculated with the following equation[145]:

$$\Gamma_{\max} = -\frac{1}{nRT} \lim_{C \to CMC} \frac{d\gamma}{d\ln C} \qquad (11)$$

where, γ denotes the surface tension, R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature, C is the surfactant concentration, (dγ/dlnC) is the slope of the γ versus lnC plot taken at cmc. The constant n takes the values 2 for conventional surfactant where the surfactant ion and centre line are univalent [119].

The area occupied per surfactant molecule (A_{min}) at the air-water interface [119] has been obtained by using following equation:

$$A_{\min} = 1/N\Gamma_{\max} \qquad (12)$$

where, N is Avogadro's number.

The surface excess concentration (Γ_{max}) of surfactant is a measure of adsorption at the air /water interface. It measures how much the air/solution interface has been changed by surfactant adsorption and depends on the molecular structures of surfactants. The maximum surface excess concentration of surfactant mixtures were obtained for anionic and cationic rich mixtures from the pre-micellar slopes of the surface tension concentration curve.

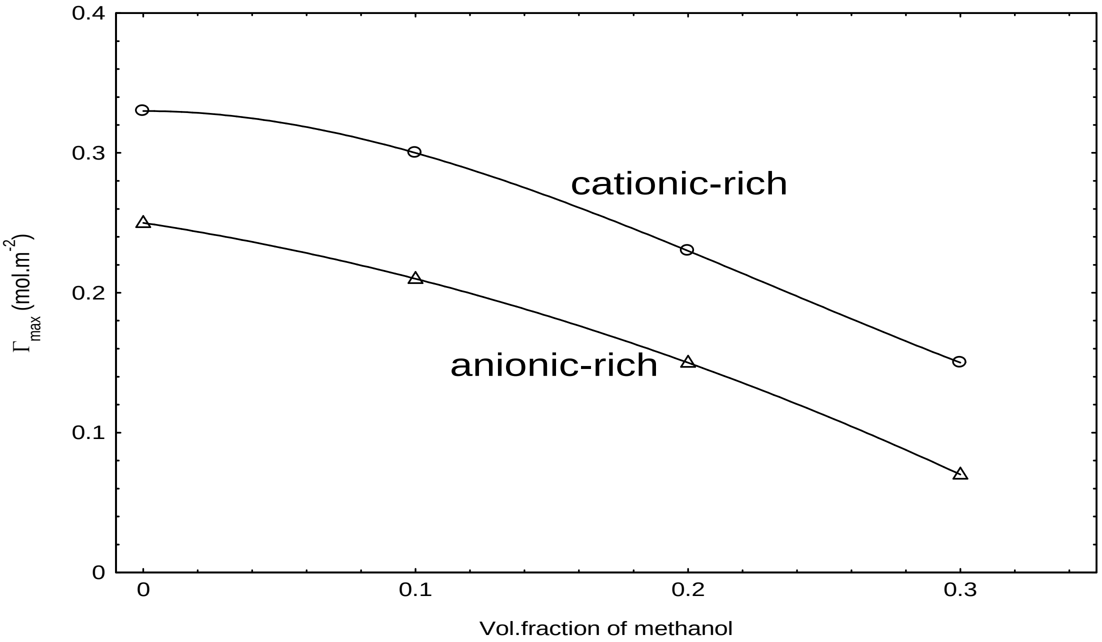


Figure 26. Variation of surface excess concentration (Γ_{max}) with the volume fraction of methanol in methanol-water mixed solvents for the surface tension measurement of anionic rich (SDS-DTAB) and cationic rich (DTAB-SDS) solutions at room temperature

Table 5. Surface properties of both the SDS-DTAB and DTAB-SDS system obtained from surface tension measurements in pure water and in methanol-water mixed solvent media containing 0.10, 0.20, and 0.30 volume fractions of methanol at room temperature

	Anionic rich		Cationic rich	
Vol. fraction of methanol	$\Gamma_{max}10^6$ (mol.m^{-2}),	A_{min} (A^2.molecule^{-1})	$\Gamma_{max}10^6$ (mol.m^{-2}),	A_{min} (A^2.molecule^{-1})
0	0.25,	658.95	0.33,	503.92
0.1	0.21,	778.31	0.30,	545.15
0.2	0.15,	1073.33	0.23,	730.11
0.3	0.07,	2318.06	0.15,	1091.76

From the above Figure (26) and table (5), it showed that the surface excess concentration decreased by increasing the methanol concentration. Methanol can breakdown the structure of water and also compete with surfactants to be exposed on the surface (changes in the water structure due to the presence of methanol, interaction between methanol and surfactant molecules and the presence of methanol at the interface can be responsible for these variations). On increasing the anionic surfactant (SDS) has the same result due to the synergism between surfactant mixtures. Similar trends were also observed by Aslanzadeh et al[145]. It is evident from the literature [145] that a water-structure breaker additive alters the surface properties of surfactants. Sansanwal [146] studied the effect of dioxane and glycerol on the surface properties of CTAB and AOT and found that there is decrease values of Γ_{max} whereas A_{min} values follow opposite trend. Due to increase in weight percent of alcohol in the mixture results in an increase in A_{min} which indicates that surfactant molecule occupies more area as methanol content is increased as illustrated in table above. The minimum area per molecule is higher for mixed surfactant systems than for either of the pure surfactants. Similar trends were found by Sohrabi et al. [147].

3.3. Density Measurement

The densities of sodiumdodecyl sulfate (SDS) in the presence of dodecyltrimethylammonium bromide (DTAB) in pure water and in three different methanol-water mixtures (containing 0.10, 0.20, and 0.30 volume fractions of methanol) and its vice-versa for the calculation of the critical micelle concentration at room temperature are presented in Figures 27-28, whereas the measured densities are reported in Appendix.

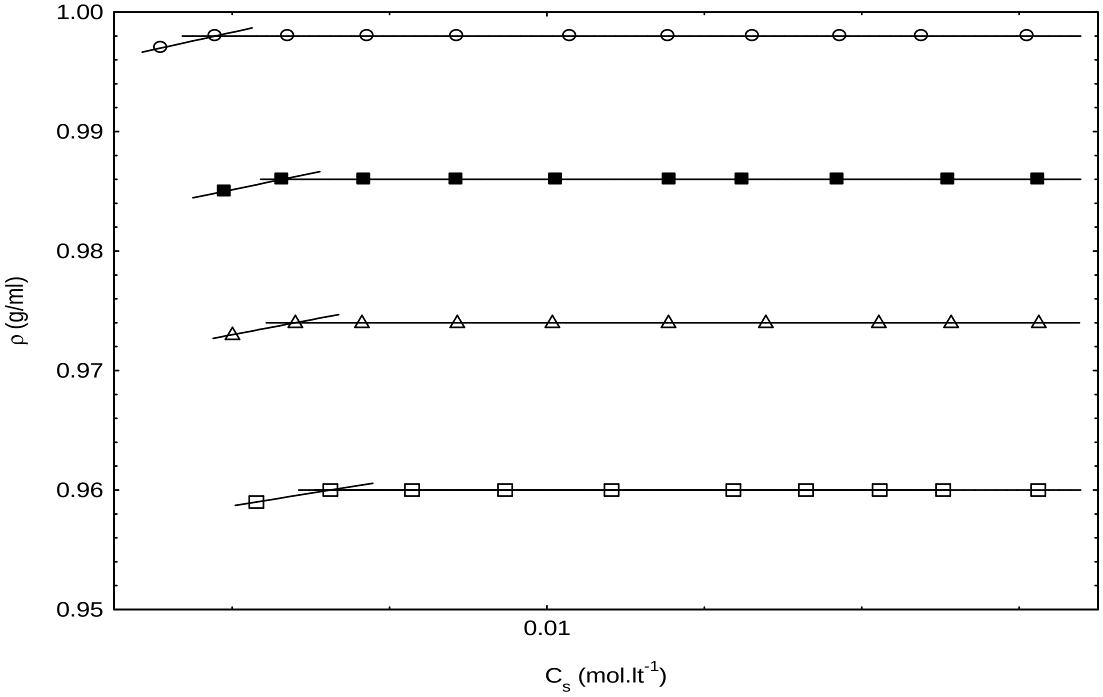


Figure 27A. Concentration dependence of density for anionic-rich mixtures (SDS in the presence of DTAB) at room temperature, in pure water (open circles) and different methanol-water mixtures (closed squares, 0.10 volume fraction of methanol; open triangles, 0.20 volume fraction of methanol; open squares, 0.30 volume fraction of methanol)

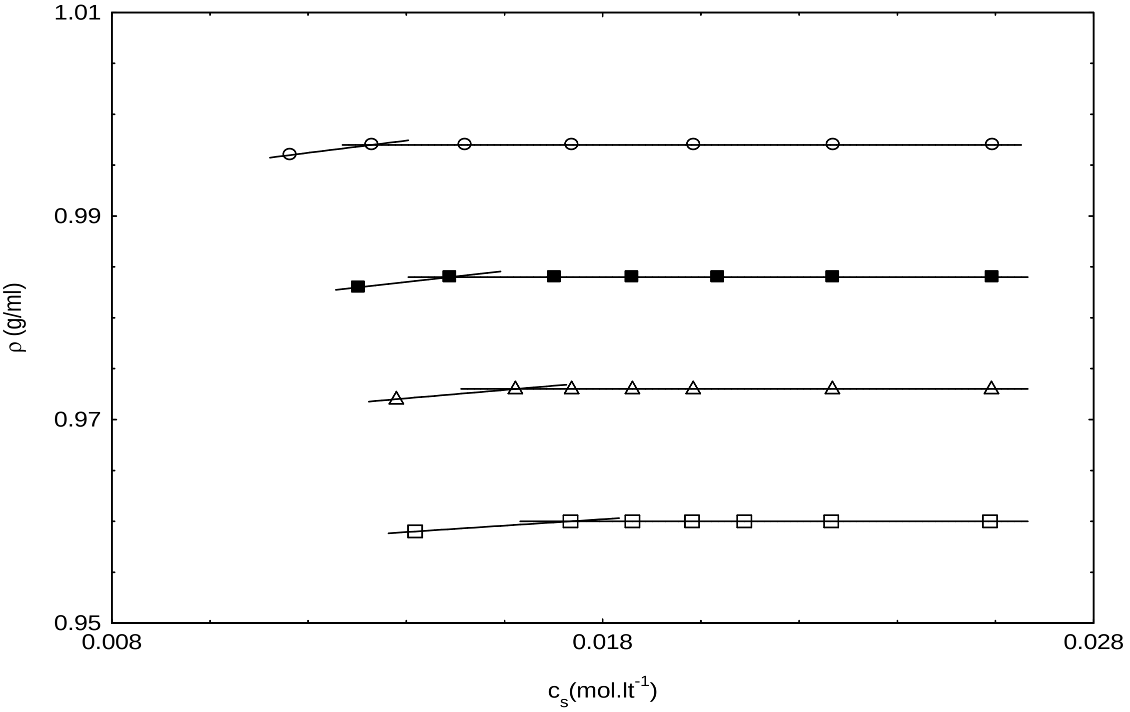


Figure 27B. Concentration dependence of density for cationic-rich mixtures (DTAB in the presence of SDS) at room temperature, in pure water (open circles) and different methanol-water mixtures (closed squares, 0.10 volume fraction of methanol; open triangles, 0.20 volume fraction of methanol; open squares, 0.30 volume fraction of methanol)

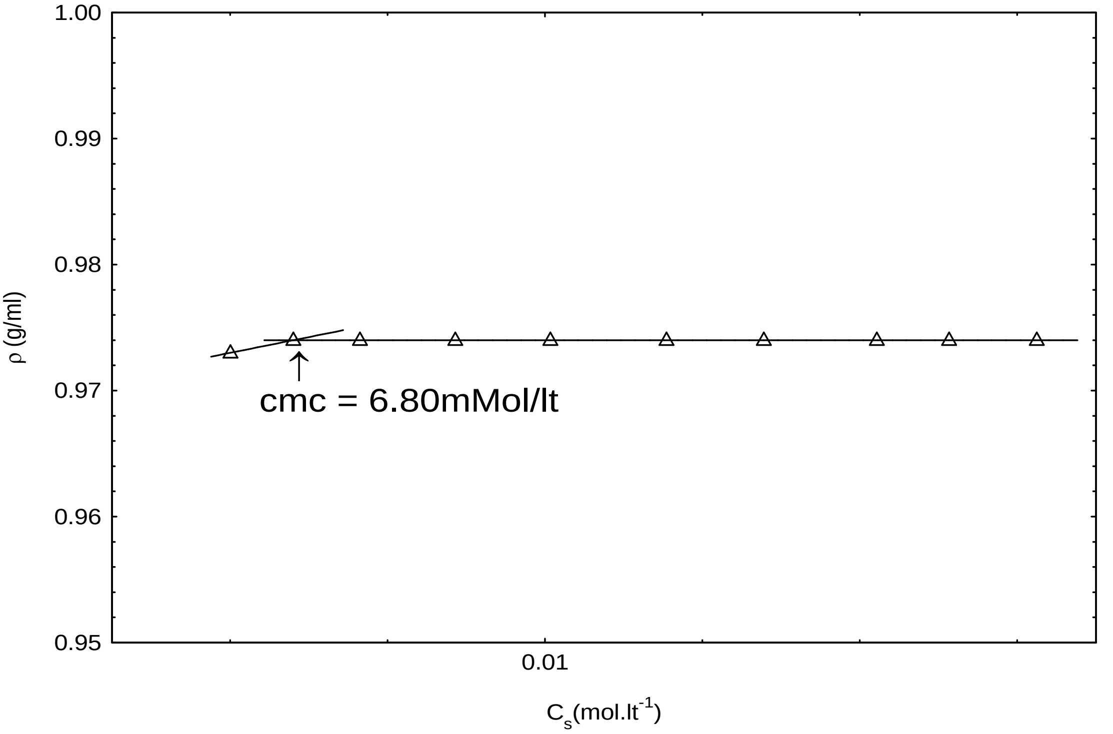


Figure 28A. Representative figure of concentration dependence of density for anionic-rich surfactant mixture (SDS in the presence of DTAB) in 0.20 volume fraction of methanol at room temperature: for critical micelle concentration (cmc) calculation

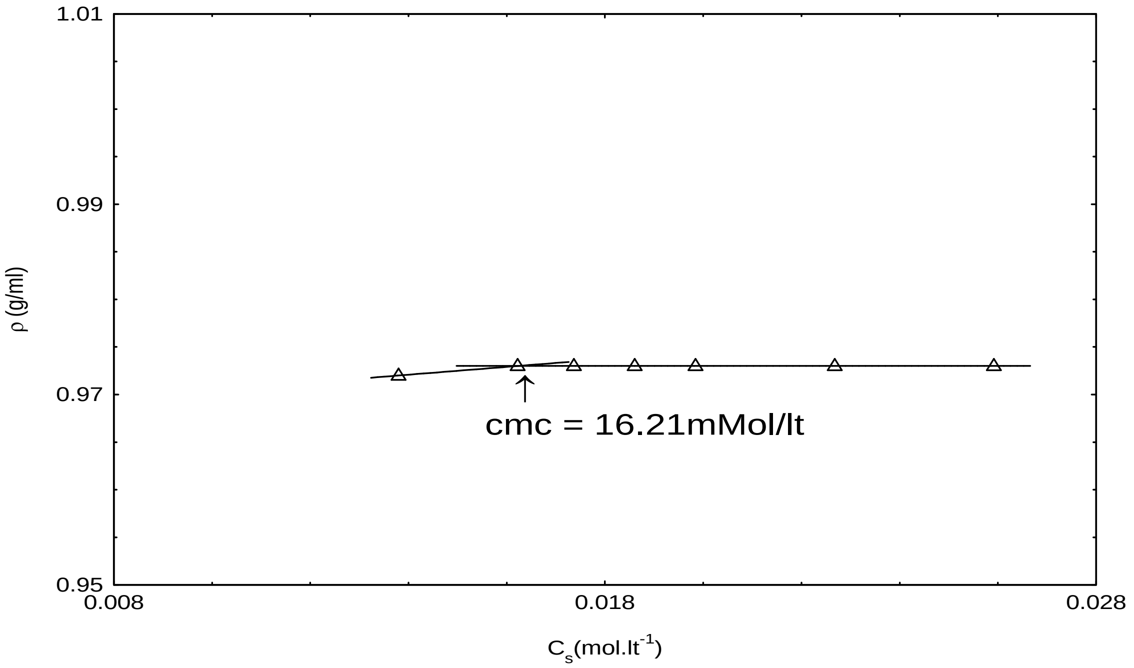


Figure 28B. Representative figure of concentration dependence of density for cationic-rich surfactant mixture (DTAB in the presence of SDS) in 0.20 volume fraction of methanol at room temperature: for critical micelle concentration (cmc) calculation

From the above figures (27-28), it is evident that densities exhibit almost increase with increasing concentration of anionic-rich (i.e. SDS in the presence of DTAB) and cationic-rich (i.e. DTAB in the presence of SDS) solutions. In fact, the variation of density with mixed surfactants concentrations are always found to be linear in higher concentration range and such trends were also observed by Bhattarai et al. [102] whereas in lower concentration range, a break can be seen and the densities decrease. Densities also decreased gradually with increase in the volume fraction of methanol for both cases. However, below the cmc the concen-tration of the mixed surfactants decreases along with the density having slopes, intercepts and correlation coefficients as shown in table 6:

Table 6. The experimental slopes, intercepts and the correlation coefficients of fits (as r^2) of anionic-rich system (SDS in the presence of DTAB) from figure (27A) in pure water and methanol-water mixtures at room temperature

Vol. fraction of methanol	Slope	intercept	r^2
0	1.45	0.990	1.00
0.1	1.37	0.977	1.00
0.2	1.25	0.965	1.00
0.3	1.06	0.952	1.00

Table 7. The experimental slopes, intercepts and the correlation coefficients of fits (as r^2) of cationic-rich system (DTAB in the presence of SDS) from figure (27A) in pure water and methanol-water mixtures at room temperature

Vol. fraction of methanol	Slope	intercept	r^2
0	0.601	0.989	1.00
0.1	0.537	0.976	1.00
0.2	0.412	0.966	1.00
0.3	0.316	0.955	1.00

Table 8. The critical micelle concentration (cmc) for both the cationic-rich (SDS-DTAB) and anionic-rich (DTAB-SDS) system obtained from density meas-urements in pure water and in methanol-water mixed solvent media containing 0.10, 0.20, and 0.30 volume fractions of methanol at room temperature

	Anionic-rich	Cationic-rich
Vol. fraction of methanol	cmc(mMol/lt)	cmc(mMol/lt)
0	5.79	13.31
0.1	6.63	14.89
0.2	6.80	16.21
0.3	7.24	17.34

Bhattarai et al[102] have only measured densities at higher concentration range of CTAB and SDS mixed system (anionic rich) in pure water and methanol water mixed solvent media but cmc has not been calculated. While here in our case new improvement has been done by measuring density in both higher and lower concentration range of mixed surfactants and cmc has been calculated and found to increase for both anionic-rich and cationic-rich mixtures in water and methanol-water mixed solvent media.

From the above table 8, it can be seen that cmc increases with the increase in the volume fraction of methanol for both the anionic-rich and cationic-rich cases.

There was no literature found for the calculation of cmc of mixed surfactants regarding density measurement. But very less literatures [122, 123] were found for the calculation of cmc of surfactants by density measurements. Gonzalez-Perez et al[122] studied the micellar properties of Octyldimethylbenzylammonium bromide in aqueous solution by density measurement at different temperatures. Janczuk et al [123] carried out density measurement and calculated cmc of two cationic surfactants: (dodecylethyldimethylammonium bromide and benzyldimethyldodecylam-monium bromide) in aqueous solutions.

3.4. Conclusions

The experimental results for the conductance, surface tension and density of salt-free solution of anionic-rich mixtures (Sodiumdodecyl Sulphate in the presence of Dodecyltrimethylammonium Bromide) and cationic-rich mixtures (DTAB in the presence of SDS) in pure water and methanol-water mixed solvent media have been presented as a function of surfactant concentration.

The conductance was found to be increased with increasing the concentration of surfactant mixtures whereas values were also found to be decreased with increasing methanol content in the mixed-solvent system. The estimation of the pre-cmc slope (S_1) and post-cmc slope (S_2) for both the anionic-rich and cationic-rich systems provides pertinent view regarding the solution behavior of mixed surfactant. The cmc and degree of micellar dissociation (α) were found be increased and the free energies of micelle formation were found to be less negative with the increasing volume fraction of methanol in a given mixed-solvent medium.

The surface tension was found to be decreased initially with increasing the concentration of surfactant mixtures in the mixed-solvent system. The cmc was found to be increased whereas the value of maximum surface excess (Γ_{max}) was decreased and minimum area per molecule (A_{min}) was followed the opposite trend i.e. increased with the increasing in methanol content in a given mixed-solvent medium.

Similarly, the density was found to be almost linear in higher concentration range while a break was seen in lower concentration range which resulted decreased in density. Density was gradually decreased with increasing in the volume fraction of methanol for both the anionic-rich (SDS-DTAB) and cationic-rich (DTAB-SDS) mixtures in a given mixed solvent medium. After cmc, visible slopes were observed and they followed the decreasing trend for both the SDS/DTAB and DTAB/SDS systems.

REFERENCES

1. Pliny the Elder, *Naturalis Historia*. Book 28, Ch. 51.
2. SDA., “Soaps and Detergents,” second edition, Soap and Detergent Association, Washington, DC, 1994.
3. Rosen M. J., “Surfactant and Interfacial phenomena”, Third edition, John Wiley &Sons, New York, 2004.
4. Romsted L. S., “Surfactant Science and Technology”, Taylor& Francis Group, CRC Press.
5. Clint H., “Surfactant Aggregation,” Chapman and Hall, New York, 1992.
6. Mc Bain J.W., *Trans. Faraday Soc.,* **1913,** *9,* 99-101.
7. Khan A., Marques E.F., *Colloid & Interface Sci.*, **2000**, *4*, 402-410.
8. Scamehorn, J. F. *Phenomena in Mixed Surfactant Systems*; Am. Chem. Soc.: Washington, DC, 1986.
9. Holland, P. M.; Roubingh, D. N. *Mixed Surfactant Systems*; Am.Chem. Soc.: Washington, DC, 1992.
10. Ogino, K.; Abe, M. *Mixed Surfactant Systems*; Marcel Dekker: New York, 1993.
11. Rosen M. J., Hua X. Y., *J.Am.Oil Chem. Soc.* **1982**, *59*, 582.
12. Lucassen- Reynders. E.H.,Lucassen J.,Giles D., *J. Colloid Interf. Sci*. **1981**, *81*, 150-157.
13. Raghavan S.R., Fritz G., Kaler E.W., *Langmuir*., **2002**, *18*, 3797-3803.
14. Hassan P.A., Bhagwat S. S., Manohar C., *Langmuir*., **1996**, *11*, 470-473.
15. Sidim T., Arda M., *J Surf Deterg*., **2011**, *14*, 409-414.
16. Salager J.L., “Surfactants Types and Uses,” second version, Merida-Venezuela., 2002.
17. Morse P.M., “Soaps and Detergents,” Chemical & Engineering News, 1999.
18. Desando M. A., Reeves L.W., *Can. J. Chem*., **1986**, *64*, 1817-1822.
19. Rosen M. J., Sulthana S. B., *J. Colloid Interface Sci.*, **2001**, *239*, 528-534.
20. Kallay N., Tomis V., Hrust V., Pieri R.,Chittofrati., *J. Colloids Surf*., **2003**, *222*, 95-101.
21. Maragoni G., Aliesha A., Mc Lachlan, *J. Colloid Interface Sci.*, **2006**, *295*, 243-248.
22. Nguyen C.M., Rathman J.F.,Scamehorn J. F., *J. Colloid Interface Sci*.,**1986**,*112*,438- 446.
23. Rubingh, D.N.; Mittal, K. L. Solution Chemistry of Surfactant; Plenum, New York, 1979; vol.1.p.337.
24. Rosen M. J., “Surfactant and Interfacial Phenomena,” second edition, Wiley, New York., 1989.
25. Rosen M. J., Dahanayake, M., “Industrial Utilization of Surfactants, Principles, and Practice,” AOCS Press, Champaign, IL, 2000.
26. Clint J. H., *J. Chem. Soc. Faraday Trans*., **1975**, *71*, 1327-1334.
27. Mukerjee P., Mysels K. J., “Critical Micelle Concentration of Aqueous Surfactant Systems,” National Bureau of Standards, Washington, DC, 1970.
28. Hadgiivanova R., Aggregation of Amphiphilic Molecules in solution: Thermo-dynamics,Metastability and kinetics. Phd. Dissertation Tel Aviv University, **2009**.
29. Lopez-Diaz D., Velazquez M.M., *J. Chem. Educ*., **2007**, *7(12)*, 327-330.
30. Chi K. A., Seung H.W., Jong M. P., *Chem Eng J*., **2010**, *158*, 115- 119.
31. Lin S., Lin Y., Chen E., Hsu C., Kwan C., *Langmuir*., **1999**, *15*, 4370- 4376.
32. Holmberg K., “Handbook of Applied surface and colloid chemistry,” J. Wiley, 2002.
33. Weber S.G., “Surfactants in Analytical Chemistry- Applications of Organized Amphiphilic Media,” Elsevier, Amsterdam, 1996.
34. Flockhart B.D., *J. Colloid Interface Sci.*, **1961**, *16*, 484-492.
35. La Mesa C., *J. Phys. Chem*., **1990**, *94*, 323-326.
36. Schick M.J., *J. Phys. Chem.*, **1963**, *67*, 1796-1799.
37. Vojtekova M., Kopecky F., Greksakova O., Oremusova J., *Collect. Czech. Chem. Commun*., **1994**, *59*, 99-105.
38. Crook E. H., Trebbi G.F., Fordyce D.B., *J. phys. Chem.*, **1964**, *68*, 3592-3599.

39. Chen L. J., Lin S. Y., Huang C.C., Chen E. M., *Colloids and Surfaces A.*, **1998**, *135*, 175-181.
40. Myers, D. Surfactant science and technology; third edition, 1946; Q D 506. M 94 2006.
41. Monduzzi M., *Curr. Opin. Colloid Interface Sci.*, **1998**, *3*, 467-477.
42. Matsuoka K., Moroi Y., *Curr. Opin. Colloid Interface Sci.*, **2003**, *8*, 227-235.
43. Blazej A. : Tenzidy, ALFA, Bratislava, 1977.
44. Mukerjee P., Mysels K.J., Kapauan P., *J. Phys. Chem.*, **1967**, *71*, 4166-4175.
45. Esposito C., Colicchio P., Facchiano A., Ragone R., *J. Colloid Interface Sci.*, **1998**, *200*, 310-312.
46. Klevens H. B., *J. Phys. Chem.*, **1948**, *52*, 130-148.
47. Dutkiewicz E., Jakubowska A., *Colloid Polym Sci.*, **2002**, *280*, 1009-1014.
48. Adam N. K., *J. Phys. Chem.*, **1925**, *29*, 87-101.
49. Hartley G. S.,"Aqueous Solutions of paraffin Chain Salts,"Hermann and Cie, Paris, 1936.
50. Moroi Y., "Micelles Theoretical and Applied Aspect," Plenum press, New York, 1992.
51. Engberts JBFN., Kevelam J., *Colloid Interface Sci.*, **1996**, *1*, 779-789.
52. Lucassen- Reyolds E. H., Lucassen J., Giles D., *J. Colloid Interface Sci.*, **1981**, *81*, 150-157.
53. Cui Z. G., Canselier J. P., *Colloid Polym Sci.*, **2001**, *279*, 259- 267.
54. Wang C., Lucy C.A., *Electrophoresis.*, **2004**, *25*, 825-832.
55. Shah, D. O.; Schechter, R. S, Improved Oil Recovery by Surfactant and Polymer Flooding; Academic press, New York, NY, 1977.
56. Dobias, B. In Phenomena in Mixed Surfactant Systems; Scamehorn, J. F, Ed.; ACS Symposium Series 311, American Chemical Society, Washington DC, 1986; p 216-224.
57. Panda A.K., Possmayer F., Petersen N. O., Nag K., Moulik S. P., *Colloids Surf.*, A **2005**, *264*, 106-113.
58. Herrington K. L., Kaler E. W., Miller D. D., Zasadzinski J. A., Chiruvolu S., *J. Phys. Chem.*, **1993**, *97*, 13792-13802.
59. Shoi A., Hatton T. A., *Langmuir.*, **2002**, *18*, 7341-7348.
60. Joshi S., Mixed Surfactant Systems: Thermodynamics and Applications in Metal Oxide Imprinting. Thesis and Dissertation- Chemical and Material Engineering, **2014**, p 29.
61. Hentze H. P., Raghavan S. R., Mckelvey C. A., Kaler E.W., *Langmuir.*, **2003**, *19*, 1069-1074.
62. Guo X., Szoka F. C., *Acc. Chem. Res.*, **2003,** *36*, 335-341.
63. Maiti K., Mitra R. N., Panda A. K., Das P. K., Rakshit A.K., Moulik S. P., *J. Phys. Chem.*, **B 2010**, *114*, 7499-7508.
64. Wang R., Li Y., Li Y., *J. Surfact Deterg.*, **2014**, *17*, 881- 888.
65. Mehreteab, A. Anionic- Cationic Mixtures; In: Broze G (ed) Handbook of Detergents, part A: properties. Marcel Dekker, New York, 1999, 133- 136.
66. Kume G., Gallotti M., Nunes G., *J. Surfact Deterg.*, **2008**, *11*, 1-11.
67. Khan, A.; Marques, E. Cationic Surfactant in Specialist Surfactant; Blackie Academic and Professional (An imprint of Chapman & Hall), London, 1997, 37- 36.
68. Umlong I. M., Ismail K., *J. Surface Sci. Tech.*, **2006**, *22*, 101-117.
69. Khan A. M., Shah S. S., *J. Chem. Soc. Pak.*, **2008**, *30*, 91- 186.
70. Niraula T. P., Bhattarai A., Chatterjee S. K., *J. Knowledge &Inn.*, **2014**, *2*, 111-113.
71. Moya M. L., Rodriguez A., Graciani M. d. M., Fernandez G., *J. Colloid Interface Sci.*, **2007**, *316*, 787-795.
72. Imai Y., Li H. H., Takumi H., Tanida H., Watanabe I., Takiue T., Mastubara H., Aratono M., *J. Colloid Interface Sci.*, **2012**, *388*, 219-224.
73. Shinoda K., Soda T., *J. Phys. Chem.*, **1963**, 67, 2072-2074.
74. Hamann S.D., *J. Phys. Chem.*, **1962**, *66*, 1359-1361.
75. Tanaka M., Kaneshina S., Shinno K., Okajima T., Tomida T., *J. Colloid Interface Sci.*, **1974**, *46*, 132-138.
76. Devinsky P.M., Lacko F.I., *Acta Facult. Pharm. Univ. Comenianae.*, **2003**, *50*, 31-119.
77. Zana R., Levy H., Dganino D., Talmon Y., Kwetkat K., *Langmuir.*, **1997**, *13*, 402-408.
78. Schulz P.C., Minardi R. M., Vuano B., *Colloid. Polym. Sci.*, **1999**, *227*, 837-845.
79. Patist A., Chabbra V., Pagidipati R., Shah R., Shah D.O., *Langmuir.*, **1997**, *13*, 432-434
80. Kato T., Takeuchi H., Seimiya T., *J. Phys. Chem.*, **1992**, *96*, 6839-6843.

81. Xiao J. X., Bao Y. X., *Chin. J. Chem.*, **2001**, *19*, 73-75.
82. Kaler E.W., Herrington K. L., Murthy A. K., Zasadzinski J. A. N., *J. Phys. Chem.*, **1992**, *96*, 6698-6707.
83. Yatcilla M. T., Herrington K. L., Brasher L. L., Kaler E. W.,Chiruvolu S., Zasadzinski J. A., *J. Phys. Chem.*, **1996**, *100*, 5874-5879.
84. Soderman O., Herrington K. L., Kaler E. W., Miller D. D., *Langmuir.*, **1997**, *13*, 5531-5538.
85. Hines J. D., *Curr. Opin. Colloid Interface Sci.*, **2001**, *6*, 350-356.
86. Gracie D., Turner., Palepu R., *Can. J. Chem.*, **1996**, *74*, 1616-1625.
87. Almgren M., Swarup S., Lofroth J. E., *J. Phys. Chem.*, **1985**, *89*, 4621-4626.
88. Pankaj S., Osamu K., Hidekazu D., *J. Colloid Polym Sci.*, **2008**, *286*, 275-282.
89. Tiwari A. K., Saha S., Saha S. K., *J. Chem. Thermodynamics.*, **2013**, *60*, 29-40.
90. Sood A. K., Singh K., Kaur J., Banipal T. S., *J. Surf. Det.*, **2012**, *15*, 327-338.
91. Matheson K. L., Cox M. F., Smith D. L., *J. Am. Oil. Chem. Soc.*, **1985**, *62*, 1391-1396.
92. Peacock J. M., Matijevic E., *J. Colloid Interface Sci.*, **1980**, *77*, 548-554.
93. Kallay N., Pastuovic M., Matijevic E., *J. Colloid Interface Sci.*, **1985**, *106*, 452-458.
94. Stellner K. L., Scamehorm J. F., *J. Am. Oil. Chem. Soc.*, **1986**, *63*, 566-574.
95. Yu Z. J., Xu G., *J. Phys. Chem.*, **1989**, *93*, 7441-7445.
96. Yu Z. J., Zhou Z., Xu G., *J. Phys. Chem.*, **1989**, *93*, 7446-7451.
97. Yu Z. J., Zhang X., Xu G., Zhao G. X., *J. Phys. Chem.*,**1990**, *94*, 3675-3681.
98. Corkill J. M., Goodman J. F., Walker T., *Trans. Faraday Soc.*, **1967**, *63*, 768-772.
99. Desnoyers J. E., Arel M., *Can J. Chem.*, **1967**, *45*, 359-366.
100. Brown G. M., Dubreulli P., Ichhaporia F. M., Desnoyers J. E., *Can. J. Chem.*, **1970**, *48*, 2525-2531.
101. Ledue P. A., Fortier J. L., Desnoyers J. E., *J. Phys. Chem.*, **1974**, *78*, 1217-1225.
102. Bhattarai A., Chatterjee S. K., Niraula T. P., *Springer Plus.*, **2013**, *2*, 280, 2-9.
103. Chauhan S., Chauhan M. S., Kaushal D., Syal V. K., Jyoti J., *J. Sol. Chem.*, **2010**, *39*, 622-638.
104. De Lisi R., Milioto S., Verrall R. E., *J. Sol. Chem.*, **1990**, *19*, 665- 692.
105. Bhattarai A., Polyelectrolyte- Surfactant Interactions in Mixed SolventMedia. Phd. Dissertation North Bengal University, 2010.
106. Park J. W.,Lee J. G., Lee H., *Bull. Korean Chem. Sco.*, **1989**, *10*, 339-343.
107. Sohrabi B., Gharibi H., Tajik B., Javadian S., Hashemianzadeh M., *J. Phys. Chem.*, **2008**, *112*, 14869-14876.
108. Aslanzadeh S., Yousefi A., *J. Surfact Deterg.*, **2014**, *17*, 709-716.
109. Rosen M. J., Hua X. Y., *J. Colloid Interface Sci.*, **1982**, *86*, 164-172.
110. Hua X. Y., Rosen M. J., *J. Colloid Interface Sci.*, **1982**, *90*, 212- 219.
111. Rosen M. J., Zhu B. Y., *J. Colloid Interface Sci.*, **1984**, *99*, 427-434.
112. Zhu B. Y., Rosen M. J., *J. Colloid Interface Sci.*, **1984**, *99*, 435-442.
113. Rosen M. J., Gu B., *Colloids Surf.*, **1987**, *23*, 119-135.
114. Tomasic V., Stefanic I., Filipovic-Vincekovic N., *Colloid Polym. Sci.*,**1999**, *277*, 153-163.
115. Mehreteab A., Loprest F. J., *J. Colloid Interface Sci.*, **1988**, *125*, 602-609.
116. Filipovic-Vincekovic N., Bujan M., Dragcevic D., Nekic N., *J. Colloid Polym Sci.*, **1995**, *273*, 182-188.
117. Lange H., Beck K. H., *Kolloid-Z.u.Z. Polymere.*, **1973**, *251*,424-431.
118. Maiti K., Bhattacharya S. C., Moulik S. P., Panda A. K., *Colloids & surf.*, **2010**, *355*, 88-89.
119. Alami E., Beinert G., Marie P., Zana R., *Langmuir*, **1993**, *9*, 1465-1467.
120. Bhattarai A., Chatterjee S. K., Jha K., *Phy. Chem.*, **2015**, *5*, 5-1.
121. Usman M., Khan A., Siddiq M., *J. Chem. Soc. Pak.*, **2009**, *31*, 221-227.
122. Gonzalez-Perez A., Czapkiewicz J., Del Castillo J. L., Rodriguez J. R., *Colloid Polym Sci.*, **2003**, *281*, 556-561.
123. Harkot J., Janczuk B., *J. Colloid & Interface Sci.*, **2009**, *330*, 467-473.
124. Bhattarai A., Nandi P., Das B., *J. Polym. Res.*, **2006**, *13*, 475-482.
125. Bhattarai A., Chatterjee S. K., Deo T. K., Niraula T. P., *J. Chem. Eng.*, **2011**, *56*, 3400-3405.
126. Umlong I. M., Ismail K., *Colloids & Surf. A. Phy. Chem. Eng. Aspects.*,**2007**, *299*, 8-14.
127. Lind Jr. J. E., Zwolenik J. J., Fuoss R. M., *J. Am. Chem. Soc.*, **1959**, *81*, 1557-1559.
128. Zana R., *J. Colloid Interface Sci.*, **1980**, *78*, 330-337.

129. Bakshi M S., *J. Dispers. Sci. Technol*., **1999**, *20*, 1715-1735.
130. Bakshi M S., *J. Macromol. Sci. Pure Appl. Chem.*, **1999**, *36*, 879-892.
131. Kaushal D., Rana D. S., Chauhan M. S.,Chauhan S., *Fluid Phase Equilibria.*, **2013**, *355*, 123-129.
132. Li W., Han Y. C., Zhang J. L., Wang L. X., Song J., *Colloid J*., **2006**, *68*, 304-310.
133. del Rio J. M., Prieto G., Sarmiento F., Mosquera V., *Langmuir.*, **1995**, *11*, 1511-1514.
134. Attwood D., Florence A. T., "Surfactant Systems: Their chemistry, pharmacy and biology," Chapman & Hall, London, 1983.
135. Zana R., *Langmuir*., **1996**, *12*, 1208-1211.
136. Moulik S. P., Haque M. E., Jana P. K., Das A. R., *J. Phys. Chem*., **1996**, *100*, 701-708.
137. Din K., Koya P. A., *J. Chem. Eng. Data*., **2010**, *55*, 1921-1929.
138. Ruiz C. C., *Colloid Polym. Sci*., **1999**, *277*, 701-707.
139. Akbas H., Kartal C., *Colloid J.*, **2006**, *68*, 125-130.
140. Das S., Mondal S., Ghosh S., *J. Chem. Eng. Data*., **2013**, *58*, 2586- 2595.
141. Chaudhary S., Pal A., *J. Mol. liq*., **2014**, *190*, 10-15.
142. Javadian S., Gharibi H., Fallah H. T., *J. Chem. Eng. Data*., **2010**, *55*, 1122-1130.
143. Dong B., Li N., Zheng L., Yu L., Inoue T., *Langmuir.*, **2007**, *23*, 4178-4182.
143. Lianos P., Lang J., *J. Colloid Interface Sci*., **1983**, *96*, 222-228.
144. Kang K. H., Kim H. U., Lim K. H., Jeong N. H., *Bull. Korean Chem. Soc*., **2001**, *22*, 1009-1014.
145. Aslanzadeh S., Yousefi A., *J. Surfact Deterg*., **2014**, *17*, 709-716.
146. Sansanwal P. K., *J. Sci & Indus Res*., **2006**, *65*, 57-64.
147. Sohrabi B., Gharibi H., Tajik B., Javadian S., Hashemianzadeh M., *J.Phys. Chem*., **2008**, *112*, 14869-14876.

APPENDIX

Table A. Conductivities of SDS in the presence of DTAB in distilled water and in three different methanol-water mixtures (containing 0.10, 0.20 and 0.30 volume fraction of methanol)

Solvent	Concentration (mol/lt)	Conductance (ohm^{-1}cm^{-1})	Solvent	Concentration (mol/lt)	Conductance (ohm^{-1}cm^{-1})
Pure distilled water	0.01325	0.707	0.10 volume fraction of methanol	0.01321	0.632
	0.01249	0.679		0.01249	0.609
	0.01156	0.645		0.01156	0.578
	0.01061	0.611		0.01089	0.554
	0.01014	0.594		0.01011	0.528
	0.00958	0.574		0.00958	0.509
	0.00893	0.549		0.00885	0.483
	0.00836	0.529		0.00836	0.467
	0.00772	0.503		0.00779	0.448
	0.00723	0.488		0.00723	0.429
	0.00677	0.471		0.00664	0.409
	0.00579	0.428		0.00564	0.360
	0.00507	0.386		0.00498	0.324
	0.00434	0.338		0.00432	0.288
	0.00376	0.301		0.00373	0.257
	0.00326	0.269		0.00329	0.232
	0.00282	0.241		0.00280	0.206
	0.00244	0.219		0.00244	0.185
	0.00207	0.192		0.00210	0.169
	0.00153	0.156		0.00158	0.137
	0.00095	0.120		0.00089	0.099
0.20 volume fraction of methanol	0.01329	0.546	0.30 volume fraction of methanol	0.01329	0.463
	0.01244	0.522		0.01221	0.433
	0.01158	0.495		0.01158	0.416
	0.01088	0.476		0.01089	0.397
	0.01017	0.454		0.01017	0.377
	0.00952	0.434		0.00956	0.360
	0.00886	0.415		0.00886	0.340
	0.00836	0.399		0.00836	0.327
	0.00775	0.382		0.00775	0.309
	0.00729	0.365		0.00634	0.262
	0.00638	0.33		0.00555	0.227
	0.00558	0.297		0.00486	0.198
	0.00488	0.262		0.00425	0.176
	0.00427	0.236		0.00372	0.155
	0.00374	0.205		0.00325	0.137
	0.00327	0.185		0.00285	0.120
	0.00286	0.167		0.00252	0.107
	0.00251	0.149		0.00221	0.095
	0.00219	0.136		0.00167	0.073
	0.00168	0.114		0.00146	0.065
	0.00101	0.083		0.00109	0.051

Table B. Conductivities of DTAB in the presence of SDS in distilled water and in three different methanol-water mixtures (containing 0.10, 0.20 and 0.30 volume fraction of methanol)

Solvent	Concentration (mol/lt)	Conductance (ohm^{-1}cm^{-1})	Solvent	Concentration (mol/lt)	Conductance (ohm^{-1}cm^{-1})
Pure distilled water	0.02819	1.95	0.10 volume fraction of methanol	0.02819	1.795
	0.02595	1.91		0.02594	1.706
	0.02271	1.76		0.02269	1.619
	0.01987	1.65		0.01987	1.504
	0.01738	1.57		0.01702	1.398
	0.01521	1.47		0.01489	1.299
	0.01331	1.36		0.01303	1.183
	0.01165	1.22		0.01140	1.06
	0.01019	1.08		0.00998	0.946
	0.00892	0.94		0.00873	0.845
	0.00780	0.83		0.00764	0.755
	0.00585	0.63		0.00668	0.674
	0.00439	0.48		0.00501	0.501
	0.00329	0.37		0.00376	0.392
	0.00247	0.28		0.00282	0.326
	0.00185	0.21		0.00212	0.263
0.20 volume fraction of methanol	0.02819	1.598	0.30 volume fraction of methanol	0.02819	1.495
	0.02592	1.522		0.02589	1.421
	0.02268	1.415		0.02265	1.318
	0.01985	1.32		0.01982	1.227
	0.01736	1.25		0.01734	1.148
	0.01519	1.107		0.01518	1.004
	0.01329	0.995		0.01328	0.901
	0.01163	0.879		0.01162	0.766
	0.01018	0.779		0.00871	0.697
	0.00891	0.688		0.01020	0.611
	0.00779	0.611		0.00779	0.547
	0.00671	0.531		0.00671	0.481
	0.00584	0.488		0.00591	0.431
	0.00483	0.399		0.00429	0.331
	0.00365	0.339		0.00349	0.281
	0.00268	0.257		0.00268	0.231

Table C. Surface tension values of SDS in the presence of DTAB in distilled water and in three different methanol-water mixtures (containing 0.10, 0.20 and 0.30 volume fraction of methanol)

Solvent	Concentration (mol/lt)	Surface tension (mN/m)	Solvent	Concentration (mol/lt)	Surface tension (mN/m)
Pure distilled water	0.00621	24.6	0.10 volume fraction of methanol	0.00663	24.2
	0.00601	24.4		0.00642	24.1
	0.00579	24.3		0.00621	23.9
	0.00562	24.2		0.00601	23.8
	0.00508	24.2		0.00543	23.7
	0.00434	24.4		0.00459	23.9
	0.00325	24.8		0.00373	24.1
	0.00242	25.1		0.00280	24.4
	0.00192	25.4		0.00210	24.7
	0.00152	25.6		0.00157	24.9
	0.00116	26.0		0.00118	25.3
0.20 volume fraction of methanol	0.00680	23.6	0.30 volume fraction of methanol	0.00775	23.8
	0.00667	23.5		0.00755	23.6
	0.00653	23.4		0.00735	23.4
	0.00640	23.2		0.00710	23.2
	0.00558	23.3		0.00642	23.0
	0.00488	23.4		0.00513	23.1
	0.00427	23.5		0.00385	23.2
	0.00374	23.6		0.00289	23.3
	0.00286	23.8		0.00213	23.4
	0.00212	24.0		0.00163	23.5
	0.00162	24.2		0.00112	23.6
	0.00120	24.5			

Table D. Surface tension values of DTAB in the presence of SDS in distilled water and in three different methanol-water mixtures (containing 0.10, 0.20 and 0.30 volume fraction of methanol)

Solvent	Concentration (mol/lt)	Surface tension (mN/m)	Solvent	Concentration (mol/lt)	Surface tension (mN/m)
Pure distilled water	0.01448	23.9	0.10 volume fraction of methanol	0.01612	23.8
	0.01409	23.8		0.01563	23.7
	0.01372	23.7		0.01513	23.5
	0.01266	23.7		0.01303	23.6
	0.01164	23.9		0.01140	23.8
	0.01035	24.1		0.00997	24.0
	0.00891	24.3		0.00873	24.2
	0.00780	24.5		0.00764	24.4
	0.00585	25.0		0.00597	24.8
	0.00438	25.4		0.00444	25.2
	0.00329	25.9		0.00330	25.7
	0.00246	26.4		0.00246	26.1
0.20 volume fraction of methanol	0.01680	23.5	0.30 volume fraction of methanol	0.01834	23.3
	0.01656	23.3		0.01795	23.2
	0.01519	23.3		0.01747	23.1
	0.01329	23.5		0.01517	23.2
	0.01163	23.6		0.01327	23.3
	0.01017	23.7		0.01161	23.4
	0.00869	23.9		0.00994	23.6
	0.00779	24.1		0.00871	23.7
	0.00584	24.4		0.00781	23.8
	0.00444	24.8		0.00597	24.0
	0.00330	25.1		0.00444	24.3
	0.00246	25.5		0.00330	24.5
				0.00246	24.8

Table E. Densities of SDS in the presence of DTAB in distilled water and in three different methanol-water mixtures (containing 0.10, 0.20 and 0.30 volume fraction of methanol)

Solvent	Concentration (mol/lt)	Density(gm/ml)	Solvent	Concentration (mol/lt)	Density(gm/ml)
Pure distilled water	0.01610	0.998	0.10 volume fraction of methanol	0.01624	0.986
	0.01476	0.998		0.01509	0.986
	0.01372	0.998		0.01248	0.986
	0.01261	0.998		0.01369	0.986
	0.01154	0.998		0.01155	0.986
	0.01029	0.998		0.01011	0.986
	0.00885	0.998		0.00885	0.986
	0.00772	0.998		0.00767	0.986
	0.00671	0.998		0.00663	0.986
	0.00579	0.998		0.00590	0.985
	0.00510	0.997			
0.20 volume fraction of methanol	0.01624	0.974	0.30 volume fraction of methanol	0.01624	0.960
	0.01513	0.974		0.01503	0.960
	0.01421	0.974		0.01422	0.960
	0.01277	0.974		0.01328	0.960
	0.01154	0.974		0.01236	0.960
	0.01006	0.974		0.01082	0.960
	0.00885	0.974		0.00946	0.960
	0.00765	0.974		0.00828	0.960
	0.00680	0.974		0.00724	0.960
	0.00600	0.973		0.00630	0.959

Table F. Densities of DTAB in the presence of SDS in distilled water and in three different methanol-water mixtures (containing 0.10, 0.20 and 0.30 volume fraction of methanol)

Solvent	Concentration (mol/lt)	Density(gm/ml)	Solvent	Concentration (mol/lt)	Density(gm/ml)
Pure distilled water	0.02595	0.997	0.10 volume fraction of methanol	0.02594	0.984
	0.02270	0.997		0.02269	0.984
	0.01986	0.997		0.02034	0.984
	0.01738	0.997		0.01860	0.984
	0.01521	0.997		0.01702	0.984
	0.01331	0.997		0.01489	0.984
	0.01164	0.996		0.01303	0.983
0.20 volume fraction of methanol	0.02592	0.973	0.30 volume fraction of methanol	0.02589	0.960
	0.02268	0.973		0.02265	0.960
	0.01984	0.973		0.02088	0.960
	0.01860	0.973		0.01982	0.960
	0.01736	0.973		0.01860	0.960
	0.01621	0.973		0.01734	0.960
	0.01329	0.972		0.01417	0.959