CHAPTER 1

1. INTRODUCTION

1.1 Introduction

Surfactants are very important substances for our daily life, as well as environment and industries (Li, 2011). In science and technology two important concerns which need to be solved nowadays, are energy and environment. For few years, the efficiency of surfactants has been increased dramatically, for example, amount of detergents which is required for cleaning effect has been reduced to one-half compared with ten years before. The amount of energy required for washing has also been decreased. Today, more than 50% of household washing is done at 30-40°C (Hovelmann, 1994). Now old nonbiodegradable surfactants are replaced by the good biodegradable and more eco-friendly surfactants. Amphoteric amino acid-based surfactants are of great interest as novel surfactants because they are used amino acids as sources which are non-toxic, bio-degradable and eco-friendly.

Soap, which is the earliest surfactant, has been used for removing dirt over 2000 years. The industrial productions of soaps were started from 19th century. Sodium stearate was the main ingredient of soap when industrial production of soap was started. Soap was gradually replaced from the market, when surfactants and detergents were synthesized in the 1930s, by using petrol derivatives as feedstock (Spitz, 2016). To satisfy various requirements as cleaners and to increase performance synthetic detergents were developed. As the soap, synthetic detergents can be used for cleaning clothes, dishes, houses, skins, hairs, etc. These surfactants have better foaming ability, lower irritating and lower temperature requirements than soap.

In the 1960s, surfactants with branched alkyl chains, which are environmentally harder to degrade, started to be replaced by biodegradable materials (Hummel, 2000). At the end of 19th century or in the beginning of 20th century, surfactants using amino acids as raw materials were applied in medical preservation. They were found to be effective against various disease-causing bacteria, tumors, and viruses (Infante *et al.*, 2003). Amino acid based surfactants were started to be used to utilize in seasonings, food additives, pharmaceuticals and elsewhere after 1988 (Takehara, 1989).Their applications in cosmetic industries were extensively investigated. Due to the development of biotechnology, some of the amino acids are being produced in a large scale by yeasts nowadays, which means the production of amino acid-based surfactants is developed to be more environment friendly.

Alkali soaps are the examples of ancient detergent. The ancestry of synthetic surfactant industries is well documented than ancient surfactants. It is difficult to point out the time period or date regarding the beginning of industry of surfactants (Karsa, 1999).At the beginning, soaps were produced by boiling animal fat, ashes of different plants containing potassium carbonate. Sulfated oils are the first well documented synthetic (non-soap) materials employed for their surface active properties (Myers, 2006).

Sulfonated castor oil produced by reacting castor oil with sulphuric acid was originally known as turkey red oil. In late nineteen-century, turkey red oil was introduced as a dyeing acid and is still used in textile and leather industries. To overcome storage of animals and vegetable fats during First World War (1914-1919 AD), traditionally classified surfactants were developed in Germany, they were the short chain alkyl naphthalene sulfonates prepared by the action of butyl or propyl alcohol with naphthalene followed by sulfonation. These showed good wetting but moderately good detergent characters and are still in use (Salager, 2002).These are still sold mainly in the United States and in Europe by different trade names. During 1920-1930 the sulfonation of long-chain alcohol became the common and resulting products were sold as the sodium salt. In United States in early 1930’s sulfonation of long chain alkyl, aryl sulfonates with benzene as the aromatic group appeared. At that time both alcohol sulfates and alkyl benzene sulfonates were used as cleaning agents but showed little impact on the general surfactant or detergent markets. After World War Second (1939-1945 AD), the alcohol sulfates were almost entirely overwhelmed by alkyl aryl sulfonates as the general cleaning agent. Later the alcohol sulfates were started to be used as the important component in shampoos and other personal care products. The developments and manufacturing of surfactants are going on continuously. In large quantities, secondary olefin sulfate derived from petroleum fractions (Myers, 2006).

After Second World War, propylene tetramer primarily a branched C_9H_{19} alkyl, $C_9H_{19}C_6H_4\text{-}SO_3^- Na^+$ coupled to benzene became a predominant material. It means alkyl benzene sulfonate (ABS) material very rapidly displaced all other basic detergents and in 1950-1965 it covered more than 50% of detergents all over the world (Myers, 2006).

Until early 1960's ABS material held almost undisputed reign as the major constituent used in the washing operation. It is found that branched alkyl benzene sulfonate is not completely bio-degradable, hence it was slowly displaced by easily bio-degradable and ecologically more acceptable straight chain alkyl benzene sulfonates or linear alkyl benzene sulfonates (Myers, 2006).

Up to 1980's, more than 75% of synthetic detergents were members of linear alkyl benzene sulfonates (LABS). In heavy duty cleaning formulation, the LABS is found 10% better than branch ABS (Myers, 2006).

In many of the areas such as detergents, cleaning products, fashion raw materials resources, the demands of ecology population growth and marketing appeal have caused the technology of surfactant to continue to grow at a healthy rate with usual up and downs that accompany most industries (Myers, 2006).

As the business of surfactants is concerned in cleaning or other operation the demand of detergent technology is increasing day by day. In our modern existence in personal care products, in pharmaceuticals, in hi-tech applications, in medicines as well as in petroleum recovery processes the surfactants are playing the important role (Kaushal *et al*., 2013). As a result, a large number of scientists and engineers with or without knowledge of surface chemistry are being called on to make use of the unique properties of surfactants (Halliday, 2005; Myers, 2006).

The term surfactant is a blend of surface active agents. Surfactants are most important chemicals available to chemists. A surfactant when dissolved in water it gives a product that has the ability to remove dirt from surfaces such as the human skin, textiles, and other solids. Each surfactant molecule has amphiphilic structure and is composed of a hydrophilic moiety (water-loving) head group and hydrophobic moiety (water-hating) tail group. The hydrophobic moiety is soluble in the oil phase while the hydrophilic moiety is soluble in the water phase. The hydrophilic groups containing the polar head groups are based on functional groups such as carboxy, sulfonate, ammonium, hydroxyl, amide, etc. Hydrophobic groups are nonpolar tails, such as hydrocarbon chain with eight to eighteen carbon atoms, and can be linear or branched. In aqueous solution hydrocarbon chain or alkyl group is called hydrophobic because it dislikes water and the polar or nonpolar head group is called hydrophilic because it likes water. The hydrophilic group attracts water molecules and hydrophobic group repels water molecules and simultaneously attaches itself to oil and grease in the dirt. These opposing forces loosen the dirt and suspend it in water. Surfactants are organic compounds which lower surface tension (or interfacial tension) between two liquids or between a liquid and a solid at relatively low concentration i.e. show surface activity (Schramm *et al.,* 2003). They are sometimes called surface-active agents, detergent or tensides, or, in the very old literature, paraffin chain salts (Schramm *et al.,* 2003). Surfactants are amphiphilic molecules i.e. they have two parts one having the affinity for nonpolar media and other part having affinity for polar media (Schramm *et al*., 2003) or having the hydrophilic head group) and hydrophobic tail group, as shown in **Figure1.1**.

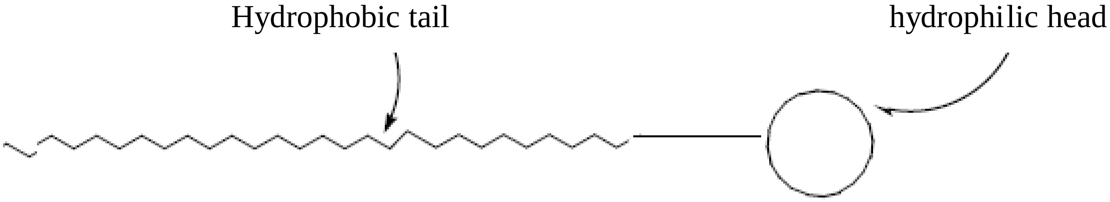


Figure 1.1: General structure of a surfactant molecule, showing hydrophilic and hydrophobic groups

Surfactants are most versatile chemicals available in synthesized compounds. Surfactant molecules oriented themselves according to their schizophrenic molecular structure and hence they adsorb at the interfaces with the polar groups towards the water and nonpolar groups towards nonaqueous phase. One of the fundamental properties of surfactants is their self-association into organized molecular structures such as micelles, vesicles, microemulsions, ellipsoid, bilayers membrane and liquid crystals (Khan *et al*., 2008). The micelle is the simplest class of association colloid it means, the cluster of surfactants ions inside the bulk of the solvent. Determination of micellization parameters like aggregation number, critical micelle concentration (cmc), etc is helpful to understand micellization characteristics of a surfactant. Surfactants have applications in many areas of biology (as membrane mimetics), pharmacy, microbiology, medicine including chemistry (Chemical Kinetics or equilibria, etc), oil recovery industry, environmental science, materials science as well as nanotechnological system (Dominguez *et al*., 1997). Selective surfactants are applicable in pesticides, spray ants, dry-cleaning, washing textile fabrics, drug disintegration, wettable packing materials and wrappers, cosmetics, surface coating doping, etc hence for industrial use more and more studies of more and more surfactants are highly useful (Singh, 2007).

Surfactants are the important component of a large number of consumer products like motor fuels, soaps, pharmaceuticals foods, etc (Tyowua *et al*., 2012). They are used to promote the dissociation of proteins from nucleic acids on extraction from biological material and in pharmacy to design drug action mechanism (Tadros, 2002).

Surfactants have 8 to 18 carbons of the straight or branched chain which is attached to a hydrophilic polar or ionic portion (Tadros, 2002). Surfactants having hydrophobic chain length 8 to 18 carbon has good but limited solubility in water. If the carbon number is more than 18 or less than 8, surfactant properties become minimal. Below 8 carbons in chain length or an alkyl group, a surfactant is very soluble and above 18 carbons in chain length or in alkyl group, it is insoluble (Guertechin, 1999). The length of chain its degree of branching, the position of the polar head group are important parameters for the determination of the physicochemical properties of surfactants (Holmberg *et al*., 2002). One of the most important properties of surfactants is that at relatively high concentration ($>10^{-4}$ M) they arrange themselves into organized molecular groups or aggregates known as micelles (Tyowua *et al*., 2012).

When surfactants dissolved slowly in water or any other polar solvent and reached to a certain value of concentration, ions or molecules of surfactants start to associate as a complex unit called micelle (Mandavi *et al*., 2008). In other words, micelles are the association of many detergent monomers that form spontaneously in solution. The simplest class of association colloids is the micelle i.e. clusters of surfactant’s ions inside the bulk of the solvent. Micellization characteristic of surfactant is understood by determining the values of its micellization parameters such as critical micelle concentration (cmc), aggregation number, etc (Khan *et al*., 2008).

Biologically active compounds or pharmaceutically active substances should soluble in water, but more than 40% of such biologically active substances are found poorly soluble. Surfactants can be used to increase the solubility of poorly soluble drugs in water and to increase drug bioavailability for the human body. Cationic surfactants of the same chain length as that of nonionic and anionic surfactants exhibited higher solubilization capacity, probably due to solubilization at the micelle-water interfaces. The solubilization of anionic surfactant SDS is less than the cationic surfactants like TTAB, DTAB, etc. This comparative study can be used to select an appropriate medium for erythromycin or other drugs solubilization (Bhattarai and Das, 2009). The solubility of a drug erythromycin (EM) was found to increase with an increase in surfactant concentration.

The surfactant is generally an organic compound which reduces the surface tension of the liquid, when presence even in very small amount. On the basis of presence and absence of charges, the surfactants are classified into ionic and non-ionic. Ionic surfactants are further classified as cationic, anionic and amphoteric (Li, 2011).

1.1.1 Anionic Surfactants

Anionic surfactants are the largest group of surfactant. They carry the negative charge on their polar head and they have good water solubility and foaming ability. Therefore, they are mainly used as the cleansing agent in many detergent formulations. The use of anionic surfactants does not have measurable environmental problems (Salager, 2002).

Most commonly used anionic surfactants are carboxylates, sulfates, sulfonates, and phosphates. Among them carboxylates are the earliest known surfactants and they constitutes the different types of soaps, e.g. sodium or potassium stearate, [$C_{17}H_{35}COOM$, (M=Na or K)], sodium myristate ($C_{14}H_{29}COONa$), sodium oleate ($C_{17}H_{33}COONa$), sodiumdodecyl benzene sulfonate [$CH_3(CH_2)_{11}C_6H_4SO_3^-Na^+$], sodiumtetradecyl-l-sulfate ($C_{14}H_{29}SO_4Na$), sodiumdodecyl-l-sulfate ($C_{12}H_{25}SO_4Na$), sodiumdioctyl sulfosuccinate, (Aerosol OT) ($C_{20}H_{37}NaO_7S$), etc (Schramm, 2009). Sulfates are mostly known anionic surfactants in which sodiumdodecyl sulphate (SDS) ($C_{12}H_{25}SO_4Na$) is probably most highly studied anionic surfactant known to science (Warra, 2013). Alkyl-sulfates are the oldest surfactants except for soaps. They are excellent foaming and wetting agents, as well as detergents and they are included in many different products for domestic and industrial uses (Salager, 2002).

Sodiumdodecyl sulfate has different synonyms like dodecylsodium sulfate,dodecyl sulfate sodium salt, lauryl sulfate sodium salt, sodiumlauryl sulfate. It is an organic compound commercially found in the form of powder or pellet. It is found that pellet form is more soluble in water and less toxic than powder form. Like all detergents, it removes oils from the skin and can cause skin and eye irritation in higher concentration. If the concentration is less than 1%, it's carcinogenic character decreases.

The sodiumdodecyl sulfate is an extremely hydrophilic surfactant. Its hydrophilicity can be reduced by adding longer chain up to C_{16} (Salager, 2002). When the electrolyte is added to the solution of SDS or temperature or pressure changes the aggregation behavior of SDS affected. The effect of aggregation behavior of ionic surfactants, due to the addition of electrolyte is mainly due to the interaction of counter ions with ionic micelle. However, there are some reports in which micellization behavior of ionic surfactants also affects by co-ions, depending on structure of co-ions and the structure of surfactants (Umlong and ismail, 2006). Experimentally it was found that cmc of SDS in presence of sodium salicylate; sodium chloride, sodium acetate, sodium propionate and sodium butyrate were found to almost same up to the concentration of 0.03 mol kg^{-1} (Umlong and Ismail, 2006). Above 0.03 mol kg^{-1} cmc of SDS in presence of sodium salicylate is found more than in presence of other salts like sodium chloride, sodium acetate, sodium propionate and sodium butyrate. It showed that cmc of SDS up to the concentration of electrolyte 0.03 mol kg^{-1} depends on counter ions as well as nature of co-ions i.e Cl^-, CH_3COO^-, etc. Salicylate is hydrotrope (compound that solubilizes hydrophobic compounds in aqueous solution) and affects the micellisation of surfactants differently than other co-ions. Due to the formation of mixed micelle in presence of sodium salicylate, the cmc of SDS is higher than other cases. Formation of mixed micelle between surfactants and co-ions is the hydrophobic not electrostatic phenomenon (Umlong and Ismail, 2006). Study of micellization behavior of SDS by using surface tension, conductance, etc. with the addition of sodium chloride, sodium acetate, sodium propionate and sodium butyrate co-ion; do not have any effect on the micellization parameters of SDS except butyrate ion, which affects the surface activity of SDS differently. Butyrate ion also shows influence on the adsorption behavior and aggregation number of SDS. Thus, it concludes that co-ion with up to four carbon atoms does not affect the cmc of SDS. Further investigation is required to ascertain the minimum number of carbon atoms required in the co-ion for showing influence on cmc of SDS (Umlong and Ismail, 2006). As other surfactants, it has an amphiphilic molecule that is containing hydrophilic and hydrophobic moiety. SDS is called carcinogenic but it is not carcinogenic when applied directly to the skin or consumed (Niraula *et al.*, 2014). It was observed that cmc of SDS in aqueous solution is 8.1×10^{-3} M at 298.15 K (Mihali *et al.*, 2008).

In sulphonate, sulphur atom is directly attached to carbon atom of alkyl group but in sulphate, the oxygen atom is indirectly attached to the carbon atom of alkyl group (Hydrophobic group) as shown in **Figure 1.2**.

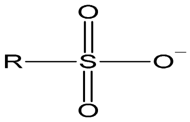


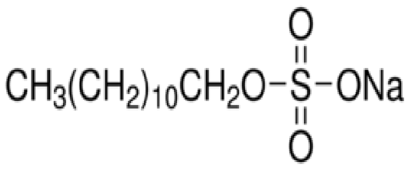
Figure 1.2: Structure of sulphonate

The most common sulphate surfactant is sodiumdodecyl sulfate and sometimes referred as sodiumlauryl sulphate (SLS) is extensively used both for fundamental studies as well as in many industrial applications (Tadros, 2002).

The salt consists of an anionic organosulfate consisting of a 12-carbon tail attached to a sulfate group, giving the material for the amphiphilic properties required of a detergent. SDS is a highly effective surfactant and is used in any task requiring the removal of oily stains and residues (Umlong and Ismail, 2007). The SDS is a synthetic detergent that differs from ordinary soaps that are produced from the hydrolysis of fats in a chemical reaction called saponification or base promoted hydrolysis of fats and oils (Warra, 2012). It is used in industrial products such as car wash soaps, engine degreasers, and floor cleaners. It is an ingredient in a wide range of personal care products such as soaps, shampoos, toothpastes, bubble-baths, washing-up liquid (dish soap), laundry detergent, children’s soaps (shampoos), stain remover, carpet cleaner, fabric glue, body washes cream, mascara, mouth wash, skin cleanser, moisture lotion, etc. It is added to soaps, bubble baths and toothpastes, etc for thickening effect and its ability to create lather and as creams and lotions. In this function, surfactants wet body surfaces, emulsify or solubilize oils, and suspend soil. It is used in so many products because it is a cheap, highly effective cleansing and foaming agent (Schaller and Hober, 1984).

In combination with antimicrobial agents, SDS can use for the treatment of cutaneous or skin infections (Piret *et al.*, 2002).The dual polarity of SDS allows it to solubilize proteins by imitating their structure. Critical micelle concentration of SDS in pure water at 298.15 K and 302.15 K are 0.0082 M and 0.0085 M respectively (Mukherjee and Mysels, 1986; Motin *et al.*, 2012). The aggregation number at this concentration at 298.15 K is usually considered to be about 62 (Turro and Yekta, 1978).

The micelle dissociation fraction (α) is 30% (Bales *et al.*, 1998). Structure and the molecular formula of sodiumdodecyl sulphate is shown in **Figure 1.3**.



$$CH_3(CH_2)_{10}CH_2O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-ONa$$

$C_{12}H_{25}SO_4Na$

Figure 1.3: Structure and molecular formula of SDS

SDS is odorless compound. Its molecular weight 288.372, density 1.01g/cm^3, refractive index (n_D) 1.461 and melting point 479.15 K. Sodiumdodecyl sulphate is a white or cream colour crystal, flake, or powder primarily used as a surfactant, emulsifier, framer, dispersant, or wetting agent in many industries, such as cleaning and personal care.

1.1.2 Caionic Surfactants

Caionic surfactants carry the positive charge on their polar head.Cationic surfactants are only 5-6% of the total production of surfactant. Cationic surfactants are extremely usefull for some specific uses, because of their typical properties.Many cationic surfactants are used as bacteriocides. They are used to clean surgery hardware, to formulate heavy duty desinfectants for domestic and hospital use. They are also used to sterilize food bottle or containers, particularly in the dairy and beverage industries.Cetyltrimethyl ammoniumbromide (CTAB) is a common cationic surfactant with molecular formula $C_{19}H_{42}NBr$ and structural formula$C_{16}H_{33}$-$N^+(CH_3)_3Br^-$(Salager, 2002). Cetyltrimethylammonium bromide has different usesone of them is as surfactant for the preparation of oil-in-water emulsions for the determination of Cu and Cr in gasoline (Santos *et al*, 2007).

1.1.3. Density

Density is a physical property of matter; it is defined in a qualitative manner as the measure of the relative "heaviness" of objects with a constant volume. Like refractive index, melting point, boiling point, vapor pressure, surface tension, conductivity, etc. Density is an intensive property. Mathematically, density is defined as the ratio of its mass to volume:

$$Density = \frac{mass}{volume} \cdots\cdots\cdots\cdots\cdots\cdots (1.1)$$

Unit of density is (g /cc) or (g/mL) in CGS and (kg/m^3) in SI unit. When methanol and water are mixed, the density is decreased with the increase in volume fraction of methanol for the methanol + water mixed solvent system (Shah *et al.*, 2014).The densities of solution increase with the increase in the concentration of solute. Increase in temperature, the density of solution decreases in all volume fraction of methanol-water mixed solvent media (Shah *et al.*, 2014).

1.1.4. Partial Molar Volume

There are different extrinsic thermodynamic properties among them is partial molar volume. The partial molar volume is helpful in the identification of solute-solute interactions as well as solvent-solute interaction. Nowadays, empirical procedures have been developed for calculation and prediction of the partial molar volume of ionic and non-ionic organic compounds in aqueous solutions (Bhattarai and Das, 2009).

The basic relation for calculation of partial molar volume, V_B, is defined by the following equation

$$V_B = (\frac{\partial V}{\partial n})_{T,P} \dots\dots\dots\dots\dots\dots (1.2)$$

Where, ∂V represent the change in total volume and n as the number of moles. The partial molar volume is often provided in units of partial molar volume cm^3/mol.

If there is concentration dependence, the partial molar volumes have to be extrapolated to concentration zero using the following equation which calculates the apparent molar volume at the finite concentrations (c).

$$V_B = \frac{M}{\rho} - \frac{10^3}{C}\left(\frac{\rho}{\rho_0} - 1\right) \dots\dots\dots\dots\dots\dots \quad (1.3)$$

Where the symbols have their usual significance and *c* is having theunit as the equivalent concentration in mol/L.

1.1.5 Study of Density and Apparent Molar Volume of Sodiumdodecyl Sulphate-cetyltrimethylammonium Bromide

The surfactants used in a multitude of industrial products, processes, and other practical applications almost always consist of a mixture of surfactants. Mixed surfactant systems are encountered in nearly all practical and industrial applications of surfactants. This is due to the natural poly-dispersity of commercial surfactants, which results from impurities in starting materials and variability in reaction products during their manufacture (Mata *et al*., 2004).Hence, one has the inherent difficulty preparing chemically and isomerically pure surfactants.

Mixed surfactant systems are much favored from the viewpoint of economy and performance. They are less expensive than isomerically pure surfactants and also they often provide better performance. Surfactant–surfactant interactions have been used extensively in industrial, pharmaceutical, technological, and biochemical fields. In the pharmaceutical field, for example, mixed micelle has been found to enhance the absorption of various drugs in human body (Tengamnuay and Mitra, 1990). A number of mixtures of cationic and anionic surfactant mixtures have been used in cleaning products to facilitate the dissolution and improved tolerance of water hardness (Ogino and Abe, 1993). Due to their synergistic behavior at *cmc*, cosmetic industries use the mixed micelles in low concentrations to avoid potential skin irritation (Garcia *et al*., 1992; Robinson *et al*., 2005; Rhein *et al*., 1990). This synergistic phenomenon can also be highly beneficial for the environment as it allows the amount of surfactant released, and hence their impact, to be substantially reduced (Kibbey and Hayes, 1997).

In view of the tremendous application potentials and economic consideration of a mixed micelle, it is necessary to search for the most suited surfactant combinations with desired requirements (such as surface activity, solubility, catalytic property, etc.). In mixed micellar systems of ionic, nonionic and zwitterionic surfactants, three types of interactions may operate, *viz*., favorable (ionic-nonionic, ionic-zwitterionic and cationic-anionic), unfavorable and ideal mixing (nonionic mixtures).

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 solutions containing two or more surfactants, the tendency of aggregated structures to form is substantially different from that in solutions having only pure surfactants. Such different tendency results in dramatic change in properties and behavior of mixed surfactants compared to that of single surfactant (Ogino and Abe, 1993).Especially, mixing of two surfactant ions of opposite charge, cationic/anionic surfactant mixtures show remarkably 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 (Jiang*et al*., 2009).

However, cationic/anionic surfactant mixtures exhibit the largest synergistic effects such as reductions in critical micelle concentration and surface tension (Menger and Shi, 2009).

The basic idea is the hydrophobicity of the salts formed by the strong interactions between two different surfactants with opposite charge. Toachieve better performance for detergent and cleaning product, mixed surfactants are commonly used to lower electrostatic forces between the surfactant heads. One of the best combinations to reduce such repulsive forces is by mixing anionic and cationic surfactants. The oppositely charged surfactants can act as counter ions to each other and thus screen the repulsive forces (Sohrabi *et al.*, 2010; Tondre and Caillet, 2001; Li and Liu, 1994).

As far as we know there is very little work in the literature dealing with the solution properties of binary mixtures of cetyltrimethylammonium bromide and sodiumdodecyl sulphate (Tomasic et.al, 1999)and no more work has been done on the effect of medium. In this work, the results are reported for density measurements on sodiumdodecyl sulphate in the presence of cetyltrimethylammonium bromide in methanol-water mixed solvent media with varying relative permittivity at different temperatures. Among various physical parameters, density and apparent molar volume have been recognized are the quantities that are sensitive to structural changes occurring in solutions (Hossain *et al.*, 2010).

In order to calculate apparent molar volumes, the solution densities are measured for sodiumdodecyl sulphate in presence of cetyltrimethylammonium bromide at the temperatures (298.15, 308.15, 318.15 and 323.15) K in pure water and in methanol + water mixed solvent media containing (0.10, 0.20, 0.30 and 0.40) volume fractions of methanol.

1.1.6. Conductance and Thermodynamic Properties

The conductometric method is frequently used for the determination of the cmc of ionic surfactant because it is simple and accurate. It is based on the fact that under normal conditions, anionic surfactant is completely dissociated (below its cmc) and there is a linear relationship between the specific conductivity, κ of the surfactant solution and its concentration as the surfactant monomers behave as normal electrolytes and thus obeying Kohlrausch’s law (Eq. 1.4) as shown below (Tyowua *et al.*, 2012).

$$K = \lambda_{\text{cation}} + \lambda_{\text{anion}}[Surfactant] \ldots\ldots\ldots\ldots (1.4)$$

All most all ionic surfactants undergo substantial slope change or break in the plot of specific conductance versus concentration (Holland and Rubingh, 1992). Above the cmc, K is constant and independent of surfactant concentration as micelles behave like weak electrolyte and (Equation -1.5) shown below is obeyed (Tyowua *et al.*, 2012).

K = ($\lambda_{\mathrm{cation}} + \lambda_{\mathrm{anion}}$ cmc) + ($\lambda_{\mathrm{cation}}$)α $[surfactant]$+ $\lambda_{\mathrm{micelle}}[micelle]$ .. (1.5)

Equation 1.5 shows that K depends on the extent of dissociation of the free surfactant monomers and the conductivity of the micelles with the concentration of the former being equivalent to the cmc. In above equation $\lambda_{\mathrm{Cation}}, \lambda_{\mathrm{Anion}}$, $[surfactant]$, $\lambda_{\mathrm{Micelle}}$ [micelle], and α represent conductivity of the cation, conductivity of anion, concentration of surfactant below cmc, conductivity of a micelle, and degree of counter ion dissociation respectively.

A plot of molar conductivity of the surfactant versus the surfactant concentration gives an abrupt change from which the cmc of the surfactant is obtained. Limiting molar conductance of solution of polar solvent increases on addition of strong electrolyte. The limiting molar conductance of NaBr is higher than NaCl. The limiting ionic conductance of Br^- is higher than the limiting ionic conductance of Cl^- in pure water as well as in propanol-water mixture of different percentage with some exception (Wypych-Stasiewicz *et al*., 2007).

The cmc can be determined by finding the break at a fixed concentration value of the plot between specific conductances versus concentration (Dutkiewicz and Jakubowska, 2002; Shanks and Franses, 1992). The ratio of slope of conductivity K versus concentration C curve above and below the cmc is called counterion binding parameter β(Shanks and Franses, 1992; Tyowua *et al.*, 2012).

Most ionic surfactants when dissolved in pure water, near the micelle concentration, they undergo self-aggregation forming micelle. In the case of SDS, with increase in surfactant concentration or on addition of salt or any other substance causes the change in size of micelle. It means aggregation number generally increases (Bales, 1998).

The specific conductance of an electrolyte solution is a measure of its ability to conduct. The SI unit of conductivity is Siemens per meter (S/m).

The conductance of a system is dependent on the cell geometry employed for the measurements,

$$C = K\frac{A}{l} \dots\dots\dots\dots\dots\dots (1.6)$$

Where $A$is the area of the electrode and$l$ is the distance between the electrodes. The parameter K is defined as the conductivity; the units of conductivity are Siemens per meter (Sm^{-1}). The conductivity of ionic surfactant is determined generally by plotting specific conductivity versus concentration. The specific conductance of a solution containing one electrolyte depends on the concentration of the electrolyte; therefore it is convenient to divide the specific conductance by concentration. This quotient is termed molar conductivity and denoted byλ_{m}, the molar conductivity is mathematically defined as:

$$\lambda_{\mathrm{m}} = \frac{K}{C} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\ldots\ldots \quad (1.7)$$

Where

K = Specific conductance and

C = molar concentration of the ion.

The unit of molar conductivity λ_{m} is $S\ m^2\ mol^{-1}$.

If we consider that ions do not interact with each other and behave as point charges, should be independent of the ion concentration. However, λ_{m} does depend on the ion concentration, for instance, due to protonation equilibria in the case of weak acids or specific interactions such as the formation of ion pairs.The conductance of a salt depends on nature and concentration of salts. The limiting molar conductance of NaBr is higher than NaCl in propanol-water mixed solvent media. The higher conductance of NaBr than NaCl is due to higher limiting ionic conductance of bromide ion than chloride ion (Wypych-Stasiewicz *et al.*, 2007).

It is well known that addition of salts greatly influences the aggregation of surfactants in solutions.Thus the solubility of salts in surfactant aqueous solutions provides basic information of surfactant aggregation in high salinity solutions. The solubility of salts NaBr, NaCl and KBr were determined at the concentrations of surfactants above and under the critical micelle concentration of SDS and the solubility of salts in SDS aqueous solutions was compared with that in water. The solubility of salts in surfactant aqueous solutions was found to increase with increasing temperature, which is similar to the solubility of inorganic salts in water. The solubility of inorganic salts in SDS aqueous solutions is much lower than that in water (Zhou and Hao, 2011).

Both intermicellar and intramicellar interaction of aqueous solution of surfactants may modify by addition of salts. The cmc and other properties are also significantly modified by adding salts. Studies of salts effect on cmc of nonionic surfactants in aqueous solution indicate that most salts lower the cmc and in most of the cases salts effect on cmc follows following relation:

$$ln_{\mathrm{cmc}} = ln_{\mathrm{cmcno\ salt}} - K_{\mathrm{S}} M_{\mathrm{S}} \cdots\cdots\cdots\cdots\cdots\cdots (1.8)$$

Where K_{S}= Salt constant, M_{S} = salt molarity (Carale *et al.*, 1994).

The cmc of SDS decreases drastically on addition of salts due to decrease of repulsion between the charged groups of SDS, hence helping the micelle to be formed at lower concentration (Valente *et al.*, 2006). Due to the absence of charge interactions, the effect of salts on cmc of non-ionic surfactants is expected to be less than ionic surfactants (Chattopadhyay and Hari Kumar, 1996). The added salts screen electrostatic repulsion between head groups and make the surfactants effectively more hydrophobic. The increased hydrophobicity interaction among the surfactants molecules causes them to aggregate at lower cmc. In another words, more micelles were formed with the addition of salt (Ataci and Sarac, 2014).

The cmc of SDS increased with increase in temperature. In alcohol-water mixture, the cmc of SDS is smaller than in pure water except in case of methanol. The value of cmc of SDS decreased with the increase in percentage of different alcohol (Ethanol, propanol, butanol, pentanol and hexanol) in alcohol-water mixture at different temperatures. The value of cmc of SDS in same volume fraction of alcohol at fixed temperature decreases with increase in chain length of surfactant (Dubey, 2008).The value of cmc of SDS changes with addition of salt but the effect of addition of cation is more than effect on addition of anion. On addition of Na^+ and K^+ from KCl and NaCl the value of cmc decreases as follows. $Na^+ < K^+$, it means value of cmc of SDS in presence of KCl is less than in presence of NaCl. The values of degree of dissociation (α) is the ratio of slope of lines above and below the cmc (Dutkiewicz and Jakubowska, 2002). The value of degree of dissociation depends on the type and concentration of the electrolyte added. In case of NaCl in presence of 0.015 to 0.1 mol

dm^{-3} salt value of (α) increases and in presence of 0.1 to 0.4 mol dm^{-3}**,** the value of (α) decreases. The anions of electrolyte cause smaller change in the values of degree of dissociation for SDS than the cations (Dutkiewicz and Jakubowska. 2002). In aqueous solution hydration of Na^+ is more than K^+ due to smaller size of Na^+ than K^+. Hence on addition of KCl, the conductivity of SDS is more than in addition of NaCl. The decrease in cmc on addition of KCl is more than in addition of NaCl (Baloch *et al.*, 2002). In pure water at 25°C, the cmc of SDS is 0.0078 mol dm^{-3} and in presence of 0.015 mol dm^{-3} NaCl and 0.015 mol dm^{-3} KCl are 0.0042 and 0.0018 mol dm^{-3} respectively (Dutkiewicz and Jakubowska., 2002).

1.1.7. Salts Effect

On addition of salts to the aqueous solution of the surfactants changes the solution properties, such as the conductance, surface tension, viscosity, critical micellar concentration, etc of the surfactant solution (Carale *et al*., 1994).

On addition of salts to the aqueous solution of colloidal electrolytes indicate that the behavior of the micellar aggregates present is not determined by Debye-Huckel relationships or the principle of ionic strength. The conductance of SDS solution increases with the addition of alkali metal salts. The variation of the cmc of SDS in presence and absence of salts as in the order: Water > NaCl > NaBr > KCl > KBr (Niraula *et al*., (2017b). Such variation in the cmc of SDS in NaCl and KCl was also found in the literature (Dutkiewicz and Jakubowska, 2002). The decrease of cmc of SDS in presence of salts has been observed. It is because the salt ions added to the solution interact with head groups of the surfactant (Kontogeorgis and Kiil, 2016). The lattice energy (kJ/mol) of NaCl = 786, NaBr =747, KCl = 715 and KBr = 682 (Reger *et al.*, 2010).The ionization potential of NaCl = 8.9, NaBr = 8.4, KCl = 8.3 and KBr = 8.0 (Batsanov and Batsanov, 2012). It was observed that the cmc increases with the increase in ionic radii of counterions (Singh *et al.*,1979) whereas Goddard et al. (Goddard *et al.*,1953)and Mukherjee et al.(Mukherjee *et al.*, 1967) reported the opposite trends that is the cmc decreases with the increase in radii as in the order radii (A°) of NaCl = 5.6405 < NaBr = 5.9732< KCl = 6.290 < KBr = 6.600 (Boer and Jordan, 1965) and the internuclear separation (A°) of NaCl = 2.820 < NaBr = 2.987 < KCl = 3.146 < KBr = 3.300 (Donnay and Ondik,1978).As in mentioned in the literature (Goddard *et al.*,1953) that Na^+ and K^+ having hydrated radius 1.78 A° and

1.22 A° with cmc of alkali metal dodecyl sulphates at 313.15 K of 0.00762 M and 0.00733 M respectively. Hence the smaller is the hydrated radii of counterions; the greater will be the lowering of the cmc. The following are the properties of the investigated monovalent salts (Table1.1).

Table 1.1: Properties of Salts (Boer and Jordan, 1965)

Salts	Ionic radii $a_{\circ}$ (A°)	Density(g/cm^3)	Mol. wt.	Lattice type
NaCl	5.6405	2.165	58.45	FCC
NaBr	5.9732	3.203	102.91	FCC
KCl	6.290	1.984	74.55	FCC
KBr	6.600	2.750	119.01	FCC

The extent of lowering of the critical micelle concentration for the formation of micelles by a salt does not depend on the number of charges on the ion of the salt which has the same sign of charge as the ion aggregate of the micelle (Corrin and Harkins, 1947). When the electrolyte is added to the solution of ionic surfactant the repulsion between the ionic head groups decreases because the electrolyte molecules insert between the ionic head groups and the monomers of surfactant can pack tightly (Staszak *et al.*, 2015).

Morphologies of the micelles are also changes by addition of electrolyte. One of the important characteristic features of the micellar solution is to form the foam and it has considerable importance in daily life, such as washing and cleaning. The presence of salt causes a significant reduction in foam volume and the rate of foam collapse is slower in presence of salt (Behera *et al.*, 2014). It indicates that on the addition of monovalent salt in the solution of SDS the lowering of cmc mainly depends on cation, not the anion because micelle of SDS is negatively charged.The cmc of SDS decreases in presence of NaCl as well as other monovalent alkali metal salts.

1.1.8. Effect of Alcohol

Methanol, as well as other alcohol, is organic additives. Organic additives or co-solvent are the very important physicochemical aspect that needs detailed investigation for both fundamental and industrial aspects. Additives such as monohydric alcohols, polyhydric alcohols, formamide, etc are water-soluble organic additives; such additives affect the micellization by altering the structure of the solvent medium, changing the relative permittivity of solvent medium and changing the hydrophobicity of the medium that alters micellization (Das *et al.*, 2013).Alcohols play a very vital role in micellization process of surfactants. The cmc of SDS increases with increase in volume fraction of methanol in methanol-water mixed solvent media. The increase in cmc with the increase in volume fraction of methanol is due to decrease in polarity of the solvent molecule and the decrease in hydrophobicity of solvent and surfactant hydrophobic part (Niraula *et al.*, 2014). The cmc of SDS decreases with increase in volume fraction of alcohol except in methanol (Kumar *et al.*, 2012). The cmc of SDS in aqueous solution decreases in presence of alcohol and further decreases with increase in the concentration of alcohol and the values of specific conductance increase with the increase in the concentration of SDS (Jain and Singh, 1981).The value of cmc obtained at (25±02°C) by conductivity measurement and potential measurement were found almost same. The data are given in Table 1.2 (Jain and Singh, 1981).

Table 1.2 The values of cmc of SDS obtained by conductivity Measurement and potential measurement at (25 ± 02°C) in water and alcohol-water mixed solvent media.

Water/Alcohol		Methods	
		By Potential measurement	By Conductance measurement
Water		8.0 mM	8.2 mM
Propanol	0.1 M	6.4 mM	5.9 mM
	0.5 M	5.8 mM	5.6 mM
	1.0 M	5.6 mM	4.7 mM
Butanol	0.1 M	6.0 mM	6.1 mM
	0.5 M	5.0 mM	5.0 mM
	1.0 M	2.8 mM	3.0 mM
Pentanol	0.1 M	5.1 mM	5.6 mM
	0.5 M	3.9 mM	4.0 mM
	1.0 M	3.0 mM	3.1 mM
Hexanol	0.1 M	4.3 mM	4.3 mM
	0.5 M	2.9 mM	3.0 mM
	1.0 M	1.1 mM	1.4 mM

The value of cmc can be determined by the study of the abrupt change in the physicochemical properties of the surfactant solution like osmotic pressure, electrical conductance, surface tension, viscosity, density, the speed of sound, light scattering, intensity, light absorption, etc. The cmc depends on many variables i.e temperature, pressure, the chain length of hydrocarbon, nature of counter ions, solvent media and different types of electrolyte added to it. The cmc decreased with increase in hydrocarbon chain length (Mahmood and Al-Koofee, 2013) and with the addition of electrolytes (Baloch *et al.*, 2002). It increased with increase in temperature, decrease in charge density of the counter ion. The cmc of SDS decreases with increase in 1-butanol content and passes through a minimum approximately at 0.5 mol kg^{-1} 1-butanol (Gunaseelan and Ismail, 2003). Addition of solvent which acts as water structure breaker like alcohol decrease the hydrophobic effect, resulting in an increase in the cmc in ionic surfactants (Gunaseelan and Ismail, 2003). In the methanol-water mixture, methanol acts as water structure breaker hence when SDS is prepared in methanol-water the cmc of SDS increases with increase in volume fraction of methanol. As mentioned above within any class of surface active agent, the cmc decreases with increasing chain length of the hydrophobic portion (alkyl group). As a general rule, the cmc decreases by a factor of 2 for ionic and by a factor of 3 for nonionic on adding one methylene group to the alkyl chain (Tadros, 2005).

1.1.9 Micelle

In scientific literature, the term micelle was introduced by a Swiss botanist Karl Wilhelm von Nageli in 1858 (Morris, 1986). Micelle was derived from Latin word mica whose meaning is crumb (a small particle of bread). James William McBain introduced the term micelle in a discussion for aggregates of soap molecules in aqueous solution (McBain, 1913). Although McBain's model has been strongly criticized it was a great improvement in colloid and interface science (Vincent, 2014).

Hydrophobic effect is the driving force for self-assembling of the amphiphilic molecules to form the micelle. Tanford introduced the term hydrophobic effect to explain the tendency of non-polar molecules to form aggregates of molecules in water (Tanford, 1980). When a non-polar molecule is placed in water, the water molecules create a cavity to accommodate the non-polar molecules. Since non-polar molecules cannot form hydrogen bonds, the creation of the cavity requires either breakage of hydrogen bonds, or rearrangement of water molecules in a way that breaking of hydrogen bonds is avoided (Privalov and Makhtadze, 1993).To understand the mechanism of surfactant solution the process of micellization is very important, it requires the study of dynamics as well as the equilibrium aspects of micellization (Cistola and Small, 1990; Daful *et al*., 2011; Love *et al*., 1984).

Micellization of surfactants in the aqueous-rich mixture is dependent on various factors like pressure, temperature, nature of solvents, turbidity, capillary electrophoresis, fluorescence, the chain length of hydrocarbon, nature of counter ions, solvent media and different types of electrolyte added in it (Kumar *et al*., 2012). As the increase in surfactants chain length at constant temperature the cmc decreases, which is directly related to the decrease of hydrophilicity of the molecules. For every surfactant, as the temperature of the system increases, the cmc initially decreases and then increases, due to the smaller probability of hydrogen bond formation at higher temperatures (Mohajeri and Noudeh, 2012).

The micelle formation or self-aggregation of ionic surfactants in solution is a resultant of two opposite processes, a supporting effect involving the removal of the non-polar mainly hydrocarbon chains from the aqueous environment and a nonsupporting effect arise from the repulsions among ionic head groups. The second effect mentioned here is reasonably pacified by the collection of counterions to the micelle surface. Salts generally decrease the cmc of ionic surfactants. The shape and size of the micelle influence by the nature of the counterions. Salts like NaCl, Na_2SO_4, etc. can convert spherical micelles of anionic surfactants to rod-like micelle. Organic factors like size of alkyl groups are also interesting. The increase in the size of the alkyl groups can decrease cmc of anionic surfactant micelles by hydrophobic interaction. The anion of the salts like., NaBr, Na-acetate, etc have been found to help the growth of spherical micelles, either acting salting in or salting out agents.

The surface charge of the micelle is partially neutralized by counterion because it is electrostatically attracted by charged micelle and adsorbing in the inner layer of micelle (Maiti *et al*., 2009). Formation of the micelle is a reversible process because dilution of the solution below the cmc eliminates micelles (Bayrak, 2003). The cmc is also an indicator of the strength at which detergent binds to protein; i.e., low values indicate strong binding and high values indicate weak binding (Wang *et al*., 2014).

The cmc is a measurement which quantifies the ability of a surfactant to form micelles, the lower the cmc, the greater the ability of the surfactant to form micelles and vice versa (Tyowua *et al*., 2012).The cmc is also an indication of a detergent's hydrophilicity (Dominguez *et al*., 1997) as shown in **Figure 1.4**.

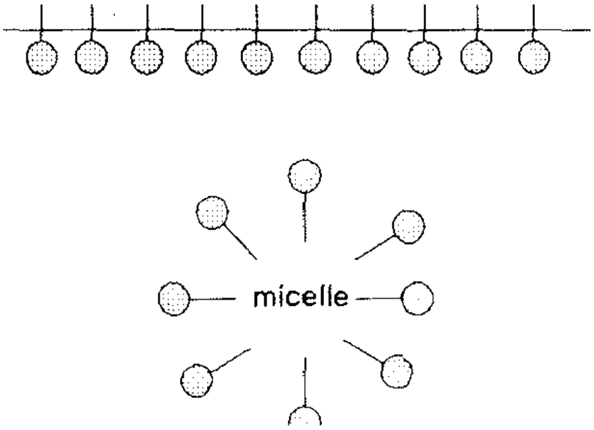


Figure 1.4: Schematic representation of surfactant molecules at surface upper and surfactant micelle in bulk liquidlower.

Figure 1.5 illustrates the situation where surfactant molecules align at the air/water interface, and form micelles.

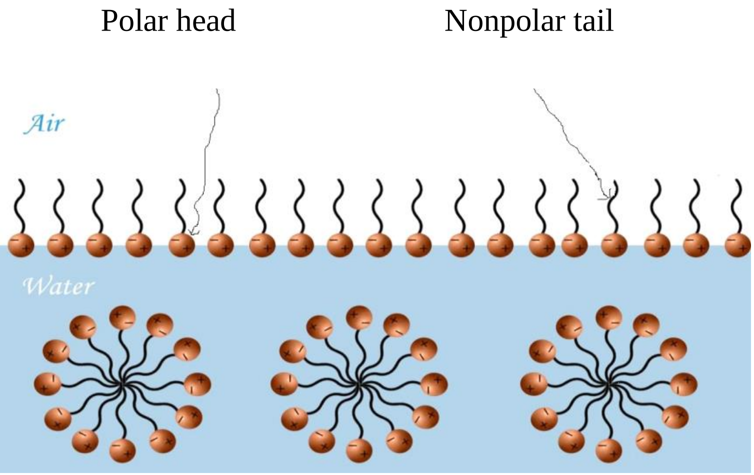


Figure 1.5: Scheme of surfactant molecules aligning on water/air interfaceand as micelle

If the solvent is ionic i.e. water or any other, the hydrophobic part of the aggregate forms the core of the micelle whereas the ionic-polar groups, such as –COO$^-$, $SO_4^{- -}$, etc oriented towards the water (Corrin and Harkins, 1947; Dominguez*et al*., 1997).The aggregates of surfactant monomer (amphiphile) form in nonpolar solvents, is generally called inverse or reverse micelles. Inverse micelles find application in different areas of modern science and technology, like for the synthesis of nano-particles and as charge control additives. The ability of surfactant inverse micelles to stabilize charge in nonpolar solvents can found in industrial uses, such as in petrochemicals as aids to disperse components and to prevent explosions.

For inverse micelles, the nonpolar hydrocarbon tail groups are towards the solvent and polar head groups aggregate into the micelle centers. Due to the formation of hydrogen bonds the intermolecular interactions in the polar solvent like in water is relatively stronger than in nonpolar solvent. The solvophobic effect driving force for reverse micelle formation in a nonpolar solvent is expected weaker than the hydrophobic effect in water (Smith *et al*., 2013).

The shape of the micelle is generally spherical but some cases it is found, conical, disk-like, rod- like, thread-like, worm-like, etc. When spherical micelles grows (e.g. by addition of salt or increasing surfactant concentration), they become either disc-like or cylindrical. When the aggregation number reaches a certain stage (Tyowua *et al*., 2012), in presence of high concentration of electrolyte the micelles of hexadecyltrimethylammonium bromide are rod like (Kushner *et al*., 1952).

By altering different factors like temperature, solvent, addition of electrolyte, etc the cmc of anionic surfactant in aqueous solution can be changed. In addition of electrolyte the cmc of surfactant decreases which depends on nature of electrolyte and concentration of the solution. The decrease in cmc is mainly to the reduced thickness of the ionic atmosphere surrounding the surfactant’s head groups and ensuing drop in electrical repulsion between them in the micelle. Evidently, the increased electrical concentration in the solution favoured this effect and hence cause a greater drop in cmc. Further decrease in cmc with addition of more electrolytes is the explanation of reduction of the ionic atmosphere around the surfactant head groups (de la Ossa *et al*., 1987). Increase in temperature beginning near zero degrees centigrade, produce the first drop in the cmc, and becomes minimum at about 25°C, then after temperature above 25°C the cmc gradually starts to increase. The reason for the change of cmc with temperature is due to different effects. One of the factor, with the increase in temperature causes the electrical interactions to weaken in the center of the solution hence the force opposed to micelle formation, are weakened, micelle formation is favored and consequently, the cmc decreased. On the other hand, the greater thermal agitation of the water molecules produces more resistance to the formation of rigid structure around the hydrophobic group of the surfactant. This causes an increase in the hydrophobic interaction and the driving force of micelle formation. However, at the same time produces an increase in water, not associated with molecules different from it, thus causing a relative decrease in the surfactant concentration making it necessary to increase concentration in order to attain the value of cmc. At low temperature, the first effect is dominant due to which the cmc decreases. At high temperature, the second factor predominates and the cmc increases (de la Ossa *et al.*, 1987).

Sodium oleate is an example of ultra-long-chain anionic surfactants, which is often used to prepare micelles with salts, cationic surfactants, or other additives (Lu *et al.*, 2014).CMC is altered by the addition of electrolyte. Above the cmc, monomers, and micelles exist in dynamic equilibrium. As shown in **Figure 1.6.**

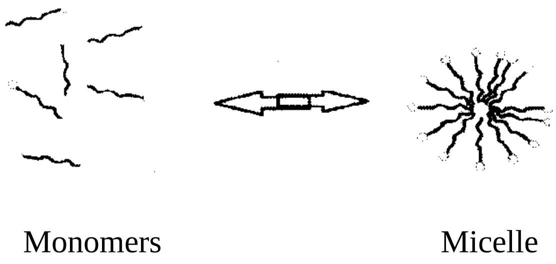


Figure 1.6: Dynamic equilibrium between monomers and micelle

The monomers–micelles equilibrium can be written as

$$nS \leftrightarrow S_n$$

Where n stands for number of monomer units, S stands for any surfactants, S_n stands for micelle formed from the surfactant monomers. Micelles are small colloidal particles, relative to the wavelength of light. When micelles form, the aqueous surfactant solution behaves as a micro-heterogeneous medium. Surfactants are completely soluble or at least partially soluble in water. Theyaccumulatemainly on the surface of the solvent and create a thin monolayer. Therefore, they are called surface-active substances as shown in previous **Figure 1.4** (Baloch *et al*., 2002). Although micelle formation is a well-known phenomenon it is very difficult to measure exact value of cmc (Khan *et al.*, 2008).

Ionic surfactants when treated with water or any other polar solvent ionizes into two types of ions (like strong electrolyte) i.e. positively charged ion called cation and negatively charged ion called anion. It means in dilute solution the surfactant acts as the normal solute. Out of two ions, only one of them is surface active. The ion which is not surface active is called counter ion (Mandavi, *et al*., 2008). For example, in sodiumdodecyl sulphate sodium ion is a counter ion and dodecyl sulphate ion is the surface active ion.

1.1.10 Micellization

Micellization is a self-assembly process that occurs in solutions of amphiphilic molecules or surfactants. In aqueous solutions above the critical micellization concentration, surfactants form insoluble crystals or micelles depending on temperature. These self-assembling structures appear across a broad range of applications, such as in drug delivery, foams and emulsions, etc. Interestingly, in the case of ionic surfactants, like SDS; the concentration and type of excess salt provide another means to control the aggregate structure and properties (Sammalkorpi *et al.*, 2009).

The surfactant in solutions above its critical micellar concentration form micelles. Micelles are considered to be micro heterogeneous in nature and they have the tendency to influence the rates of reactions. The ability of micelles to catalyze both (positive and negative) reaction rates depends on the nature of the interactions between the surfactant and reactants. Micelles influence the reaction rates by localization, delocalization or dispersion of charges in the ground state and transition state of the substrate. It believes micelles mimic the enzymes structurally and functionally. Sodiumdodecyl sulphate and Brij-35 inhibit the rate of hydrolysis of derivatives of acetaminophen (Al-Blewi *et al.*, 2014).

Usually, ionic amphiphiles form small nearly spherical micelles at low ionic strength. When one increases the concentration of counter ions, some ionic concentration and the aggregation number can increase up to 20 folds and the micelle is above interpreted to undergo a sphere to rode shape transition (Motin, *et al.,* 2012). Determination of cmc of the aqueous solution of SDS by static or dynamic light scattering technique in presence of 0.8 M NaCl at 303.15 K was found that aggregation number in the ranges from 60 to 1000.The aggregation number dramatically decreases at the higher temperature. In fact, at 353 K the micelles are small with aggregation number around 100 where the concentration of NaCl is 0.8 M (Chan et al., 1986).

1.1.11 Thermodynamic Properties

The thermodynamic property standard Gibb's free energy of micellization, $\Delta G^{\circ}_{\mathrm{m}}$ can calculate by the relation.

$$\Delta G^{\circ}_{\mathrm{m}} = (2-\alpha)\ RT lnX_{\mathrm{cmc}} \ldots\ldots\ldots\ldots\ldots\ldots (1.9)$$

Where X_{cmc} mole fraction of surfactant at cmc, R is universal gas constant and T is the temperature.

The standard enthalpies of micelle formation, $\Delta H^{\circ}_{\mathrm{m}}$can calculate from Gibbs-Helmholtz equation

$$\Delta H^{\circ}_{\mathrm{m}} = -T^2 R\ (2-\alpha)\left[\frac{\partial lnX_{\mathrm{cmc}}}{\partial T}\right]_{\mathrm{p}} \ldots\ldots\ldots\ldots\ldots\ldots (1.10)$$

The term$\left[\frac{\partial lnX_{\mathrm{cmc}}}{\partial T}\right]_{\mathrm{p}}$ can calculate by fitting the plot of lnX_{cmc} versus temperature. From the values of $\Delta G^{\circ}_{\mathrm{m}}and\Delta H^{\circ}_{\mathrm{m}}$.The standard entropy of micellization, $\Delta S^{\circ}_{\mathrm{m}}$can calculate by using standard Gibb's free energy of micellization and standard enthalpies of micelle formation,

$$\mathrm{T}\Delta S^{\circ}_{\mathrm{m}} = \Delta H^{\circ}_{\mathrm{m}} - \Delta G^{\circ}_{\mathrm{m}} \ldots\ldots\ldots\ldots\ldots\ldots (1.11)$$

The variation of both $\Delta H^{\circ}_{\mathrm{m}}and\Delta S^{\circ}_{\mathrm{m}}$ values show the enthalpy-entropy compensation effect.When the enthalpy contributes less to $\Delta G^{\circ}_{\mathrm{m}}$, its counterpart noted as $\Delta S^{\circ}_{\mathrm{m}}$, contributes more.

A linear relationship is obtained for $\Delta H^{\circ}_{\mathrm{m}} - \Delta S^{\circ}_{\mathrm{m}}$ and is expressed with the help of Equation. (1.12).

$$\Delta S^\circ_\mathrm{m} = \frac{1}{T_\mathrm{c}}\Delta H^\circ_\mathrm{m} + \sigma \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.12)$$

Where σ is intercept of linear plot and $1/T_\mathrm{c}$ is the slope of the compensation plot.T_c is the compensation temperature, can be interpreted as a characteristic of solute-solute and solute-solvent interactions, i.e., proposed as a measure of the "desolvation" part of the process of micellization. The intercept σ characterizes the solute-solute interaction, i.e., considered as an index of the "chemical" part of the process of micellization (Chen *et al.*, 1998). The increase in σ corresponds to a decrease in the stability of the structure of the micelles.

Temperature dependence of hydrophobic effect expressed as heat capacity of micellization$\left(\Delta_\mathrm{m} C^\circ_\mathrm{p}\right)$ and estimated from slope of $\Delta H^\circ_\mathrm{m}$ versus temperature curve for surfactants solution is noted as under

$$\Delta_\mathrm{m} C^\circ_\mathrm{p} = \frac{\partial \Delta_\mathrm{m} H^\circ}{\partial T} \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.13)$$

The negative values of $\Delta_\mathrm{m} C^\circ_\mathrm{p}$ observed for the self-association of amphiphiles and can be recognized to the removal of large areas of the nonpolar surface from contact with water on micelle formation.

The free energy of surfactant transfer; $\Delta G^\circ_{\mathrm{trans},}$can calculate by the relation

$$\Delta G^\circ_{trans} = (\Delta G^\circ_\mathrm{m})\ (methanol + water) - (\Delta G^\circ_\mathrm{m}) water \ldots \quad (1.14)$$

1.1.12. Correlation of $\Delta G^\circ_\mathrm{m}$ with Solvent Parameters

Various solvent parameters have been used to describe the characteristics of a liquid as a solvent. Three solvent parameters are important in our study. They are Reichardt's parameter, Hildebrand parameter and Gordon parameter. Values of Reichardt's parameter [E_T(30)] are known for several hundred solvents, and are obtained from the peak wave number of the longest wavelength charge transfer absorption band of the betaine indicator 2,6-diphenyl-4- (2,4,6-triphenyl-1-pyridino)-phenoxide in dilute solution in the solvent (Dawber *et al.*, 1988). This indicator, which was number 30 in a series of compounds studied, hence the designation E_T(30), exhibits a very high sensitivity to solvent polarity, i.e., a very wide range of wavelengths of the hypsochromic or blue-shift effect in solvents of increasing polarities.

Hildebrand proposed a solubility parameter, δ, which is a numerical value that indicates the relative solvency behavior of a specific solvent (Hildebrand and Scott, 1964). The Hildebrand solubility parameter is defined as the square root of the cohesive energy density: $\delta = (E/V)^{1/2}$ where V is the molar volume of the pure solvent, and E is its measurable energy of vaporization. The Hildebrand parameters are applicable to regular solutions, which, in the current context, imply strictly nonpolar systems. In our context, the Hildebrand parameter can be calculated by using the relative permittivity of the solvent.

Hildebrand-Hansen parameter values for water-organic solvent mixtures are scarce in the literature. A quantity with analogous meaning to the Hildebrand-Hansen solubility parameter is the relation $\gamma/V^{1/3}$ proposed by Gordon (Sjoeberg*et al.*, 1990), where γ is the surface tension and V is the molar volume of the solvent. The ability of a determined liquid to bring about the self-association of conventional amphiphiles can be characterized by its Gordon parameter, *G*. This parameter is considered to be a measure of the cohesive energy density of the solution.

The correlation of $\Delta G_\mathrm{m}^\mathrm{o}$ with relative permittivity, Reichardt's parameter, the Hildebrand parameter and the Gordon parameter are very famous nowadays in mixed solvent system.

The Hildebrand parameter, δ values can be calculated with the popular relationship (Paruta *et al*., 1962; Lordi *et al*., 1964; Marcus, 1985).

$$\delta = 0.45D + 18.5 \quad \dots\dots\dots\dots\dots\dots (1.15)$$

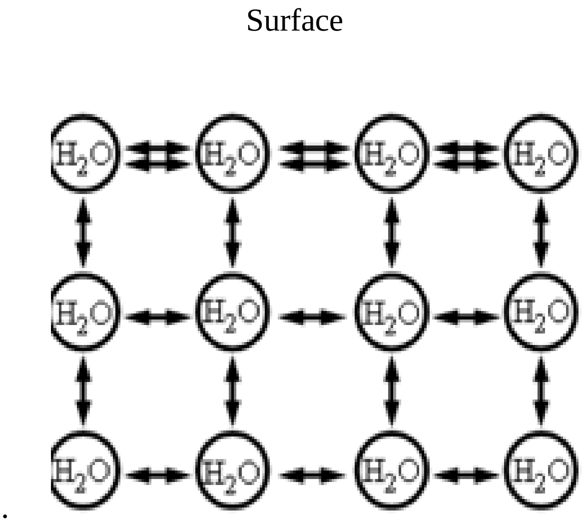
1.1.13. Correlation of $\Delta G_\mathrm{m}^\circ$ with Solvophobic Parameter (S_p)

The solvophobic parameter, S_p, iscalculated by Gibbs energies of transfer (Abraham *et al*., 1988).The correlation method developed by (Wang *et al.*, 2011) with which the S_p values of the mixed solvents can be calculated. The solvophobic parameter of water is high whereas decreases with the addition of methanol.

1.1.14 Surface Tension

The meaning of surface tension is a chemical phenomenon that happens at the surface of a liquid where the liquid becomes denser than the rest. The presence of dissolved solute or impurities on the surface affects the surface tension of the liquid. The presence of highly soluble substances increases the surface tension of water or any other solvent, whereas sparingly soluble substances reduce the surface tension of water or any other solvent. The surface tension of liquid decreases with increase in temperature (de Castro *et al*., 1998).

The surface tension of a liquid is defined as the energy required for breaking through the surface. Liquids like water, which have strong molecular interactions have high surface tensions. The term surface tension is generally used in liquids. Surface tension has the significant effect on day to day existence as well as the survival of living beings. For example, insects such as water striders depend on the surface tension of water to move around and to take food. Most of the detergents used in different activities contain sodiumdocedyl sulfate (SDS) which reduces the surface tension of water. If in water any surfactant or detergent is added and reaches a specific concentration of detergent or surfactant, water striders will break the surface tension and sink. Surface tension is also essential for the transfer of energy from wind to water to create waves. Waves are necessary for rapid oxygen diffusion in lakes, ponds, seas, etc. The liquid molecules in the surface are differently attracted by surrounding molecules than the molecules in bulk or inner surface. The molecule in inner surface are equally attracted by other molecules around it by van der Waals force or by force of cohesion but the surface molecule is unequally attracted due to lack of liquid molecules above the surface as shown in **Figures 1.7, 1.8 and 1.9.** The unequal pulls of the surface molecule due to van der Waals force or by force of cohesion towards the centre and other sides for surface molecule results in the surface tension**.** The contracting force on the surface is called surface tension (Lower, 2009).



Surface tension-molecules at the surface form strong bonds

Figure 1.7: Water molecules showing surface and bulk molecules

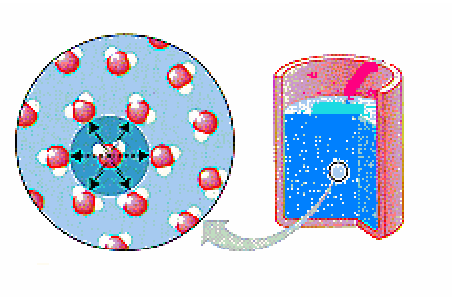


Figure 1.8: Water molecules showing bulk molecule

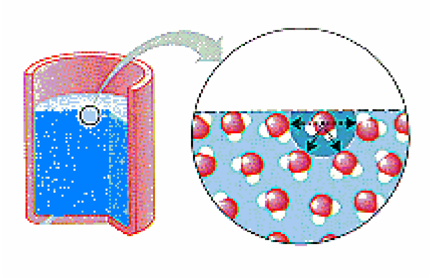


Figure 1.9: Water molecules showing surface molecules

Figures 1.7, 1.8 and **1.9** shows that the surface molecules of liquids are strongly attracted by central molecules than the air molecules above it, therefore, the surface molecules are strongly bonded with surrounding liquid molecules by a particular force which is known as surface tension. The phenomenon of surface tension is responsible for cohesive forces or van der Waals force between the liquid molecules. The surfaces molecules of liquid cohere to the molecules directly associated with the molecule more strongly. The surface molecules which are in under tension behave like an elastic membrane.

On addition of surfactants, the surface tension of liquids or solvents decreases. Due to their hydrophilic structure, surfactant molecules spread or arrange in solvents such as water in such a way that their concentration in bulk is less than that in the liquid-gas interface of the solution. At the interface, the molecules are arranged in such a way that the polar groups pointing toward the polar phase, while their nonpolar, or hydrophobic, groups point away from the polar groups of solvent. Adsorption of a large amount of molecule at the liquid-air interface causes a gradual decrease in the solvent surface tension even at very low surfactant concentrations such decrease in surface tension is quite considerable. Such surface activity depends on different factors like the nature of surfactant, the nature of solvent, the structure of solvent, temperature, pH, etc. Surface tension is inversely proportional to the concentration of surfactant as well as the temperature of solution (de Castro *et al.,* 1998). The unit of decrease of surface tension depends on the concentration of surfactant. In very dilute solution, the surface tension is almost same to that of the pure solvent. With the increase in concentration more and more surfactant is able to stabilize the surface, due to lowering the surface tension. Slow addition of more amount of surfactant in solution at a particular point the surface tension of solution remains almost constant, which indicates critical micelle concentration. This is because, at critical micelle concentration, the surfactants reach their saturation point in the liquid and begin to self-associate (starts to form micelles) in the liquid phase. Any additional surfactant that is added after this point will add to the micelles thus will not further increase the surface stabilization. The result is that a graph of surface tension versus surfactant concentration will show two types of behavior above and below the cmc. Surface tension can measure with the help of Stalagmometer or Survismeter (Singh, 2007).

The maximum surface excess concentration $\Gamma_{\max}$, has been calculated by using Gibb's isotherm,

$$\Gamma_{max} = -\frac{1}{2.303\,nRT}\left[\frac{\partial\gamma}{\partial log\mathrm{C}}\right]_{TP} \cdots\cdots\cdots\cdots\cdots\cdots (1.16)$$

Where γ denotes the surface tension, R denotes universal gas constant (8.314 $\mathrm{Jmol^{-1}\,K^{-1}}$), T denotes the absolute temperature and C denotes surfactant concentration. Here $\left[\frac{\partial\gamma}{\partial log \mathrm{C}}\right]$ is the slope of the γ versus *log* C plot taken at cmc. The constant '*n*' takes the values 2 for conventional surfactant where the surfactant ion and the counter ion are univalent (Alami *et al*., 1993; niraula *et al*., 2017a).

The area occupied per surfactant molecule (A_{min}) is calculated by,

$$A_{\mathrm{min}} = \frac{1}{NT_{\mathrm{max}}} \dots\dots\dots\dots\dots\dots (1.17)$$

Where N is Avogadro's number.

The value of the surface pressure at the cmc (π_{cmc}) is obtained by the relation

$$\pi_{\mathrm{cmc}}=\gamma_0 - \gamma_{\mathrm{cmc}} \dots\dots\dots\dots\dots\dots \quad (1.18)$$

Where γ_0 and $\gamma_{\mathrm{cmc}}$are the values of the surface tension of water and the surfactant solution at the cmc respectively. The surface excess concentration (Γ_{max}) is an effective measure of adsorption at 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 standard free energy interfacial adsorption at the air/saturated monolayer interface can calculate by the relation.

$$\Delta G^{\circ}_{\mathrm{ads}}=\Delta G^{\circ}_{\mathrm{m}} - \frac{\pi_{\mathrm{cmc}}}{\Gamma_{\mathrm{max}}} \dots\dots\dots\dots\dots\dots (1.19)$$

The packing parameters, P can determinethe relation

$$P = \frac{V_0}{A_{\mathrm{min}} l_{\mathrm{c}}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.20)$$

Where V_0 is the volume of exclusion per monomer in the aggregate, according to Tanford's formula (Tanford, 1980).

V_0= [27.4 + 26.9 n_{c}]Å^3,

l_{c}= [1.54 +1.26 n_{c}] Å is the maximum chain length and n_{c} is the number of carbon atoms with hydrocarbon chain. The A_{min} refers to the property related to the surfactant monolayer at the air/water interface. The packing parameters 'P' determine the geometry of micelles and indicate minimum sized aggregates in solution, which minimizes the Gibbs free energy of micellization.

1.1.15. Viscosity

The term "viscosity" is derived from the Latin "Viscum", meaning mistletoe. Viscosity is another property of surfactants which can be used for the measurement of cmc. Viscosity is defined as the internal resistance or friction of liquid or gas to flow. It is one of the most important properties of fluids and has a very important role in the petroleum industry. When two or more than two liquids flow on the same surface then they move with different rates or they have different viscosities. The liquid which moves faster is known as less viscous and which moves slower is known as more viscous.

Viscosity is due to the friction between neighbouring particles in a fluid that is moving at different velocities. If a liquid (fluid) is flowing through a tube in such condition the liquid near the axis generally moves faster than the liquid near the walls. It shows that some stress is needed to overcome the resistance between the layers and keep the fluid moving. A fluid that has no resistance to shear stress is known as an ideal fluid or inviscid fluid. A liquid whose viscosity is more than that of water is known as a viscous liquid, while a liquid with a viscosity less than water is called a mobile liquid.

Viscosity B coefficient shows the interaction between solute and solvent and viscosity B coefficient gives by Jones-Dole equation (Kay *et al.*, 1966).

$$n_{\mathrm{r}} = 1 + A\sqrt{C} + BC \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.21)$$

Where $n_{r=}\frac{n}{n_0}$ = the relative viscosity of a solution and A and B are constants.

Equation 1.21 can be rearranged as

$$\frac{n_{\mathrm{r-1}}}{\sqrt{C}} = A + B\sqrt{C} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.22)$$

The viscosity of liquid can measure by using Ostwald's viscometer or Survismeter (Singh, 2007).The viscosity of a liquid can determine by measuring flow time for the fixed volume of it and the fixed volume of other liquid whose viscosity is known in suitable apparatus and comparing their flow time.The viscosity of a surfactant increases with the addition of salts like NaCl, but after the certain concentration of salt the value of viscosity decreases. When the viscosity of a solution of a liquid is plotted against the logarithm of the concentration of the surfactant it gives a curve. When two lines are drawn by using the curve, at a particular point two lines meet that meeting point of the curves is known as cmc.

1.2. Rationals of the Study

Due to lack of detailed study of surfactants treatment of different diseases are still very costly and even some are almost impossible. The durability of structures made of iron and steel are not as more as expecteddue to corrosion. The productivity of different agricultural plants and their lifetime are also necessary to improve. The cleansing efficiency of surfactants is not sufficient to fulfill demands of existing developing world. In the field of cosmetics demands of surfactants are growing day by day. To overcome all problems mentioned here and others precise study of surfactants is necessary.

This research is carried out to study the effect of the change in hydrophobicity with the addition of four different volume fractions of methanol on the micellization of SDS in presence and absence of some alkali metal halides at four different temperatures. In this study, the changes in thermodynamic properties, solvent parameters, solvophobic properties, surface properties and interaction of solvent with the micelle are also included. Mixed surfactant systems are much favored from the viewpoint of the economy. Surfactant–surfactant interactions have been used extensively in industrial, pharmaceutical, technological, and biochemical fields.

1.3. Objectives

1.3.1. General Objectives

To find new uses of or to improve the different existing uses of SDS.

1.3.2. Specific Objectives

1 To study the densities of SDS solutions in pure water, and different volume fractions of methanol at different temperaturesand to investigate the partial molar volume.

2 To study the densities of SDS-CTAB solution in pure water, and different volume fractions of methanol at different temperature and to investigate the apparent molar volume. F

3 To study the conductivities and related thermodynamic parameters of SDS solutions in pure water, and different volume fractions of methanol at different temperature in presence and absence of additives.

4 To study the variation of the standard free energy of micellizations ($\Delta G^{\circ}_{\mathrm{m}}$) with the solvophobic parameters (S_{p}).

5 To study the surface tensions and some of the related surface properties of SDS solutions in pure water and different volume fractions of methanol at different temperatures.

6 To study the viscosities and related related B coefficientsof SDS solutions in pure water, and different volume fractions of methanol at different temperatures.

CHAPTER 2

2. LITERATURE REVIEW

Surfactants have applications in many areas such as Biology, Pharmacy, Microbiology, Medicine, Chemistry, Industries, Environment, Materials science as well as Nanotechnological system (Dominguez *et al.*, 1997). Surfactants having hydrophobic chain length 8 to 18 carbons have good but limited solubility in water. Surfactants are used in all most all sectors of modern industries; such use of the surfactant is due to its self-association phenomenon (Khan and Shah 2008). Surfactants are completely or at least partially soluble in water. They accumulate mainly on the surface of the solvent and create the thin monolayer, therefore, they are called surface-active substances (Baloch *et al.,* 2002). In dilute solution, the molecules or ions of surfactants are moving freely, but when concentration increases such molecules or ions starts to associate themselves after certain concentration. In dilute solution, the surfactant acts as normal solute and ionized into two types of ions they are cation and anion. Out of two ions, only one of them is surface active, the ion which is not surface active is called counterion (Mandavi, 2008). Surfactants have found a wide range of applications such as detergency, solubilization and surface wetting capabilities.They are also applicable in mining, petroleum and pharmaceutical industries, biochemical research and as catalysts in several organic and inorganic reactions (Fendler and Fendler, 1975).

Anionic surfactants are the largest group of surfactant. Anionic surfactants are used as very important molecules in detergency, emulsion and other industrial fields (Schramm, *et al*., 2003; Rafati and Maleki, 2007). Most commonly used anionic surfactants are carboxylates, sulphates, sulphonates and phosphates. SDS has protein denaturing power. It has been found to inhibit the effect of sexually transmitted diseases (STD). Repeated administrations of SDS on the vaginal mucosa of rabbits show that SDS is well tolerated by them. SDS could use as an efficient chemical for the topical microbicide to control the transmission of sexually transmitted pathogens. In combination with antimicrobial agents, SDS could also be used for the treatment of cutaneous or skin infections (Piret *et al.*, 2002). SDS has huge application in industries and biosurfactants. SDS is applicable in agriculture, industries, mines and oil recovery as well as wetting, foaming and emulsifying agent in cosmetics and pharmaceutical products (Noudeh, *et al*., 2007a; Noudeh, *et al*., 2007b).

SDS is anionic surfactant used most frequently having the negative charged head-group balanced by a positively charged counterion sodium (Mitsionis andVaimakis, 2012). SDS can also use as the additive for the removal of fly ash from the slurry (Singh, 2012). SDS has different important industrial applications like engine degreaser, foaming agent, cleaner, etc (Warra, 2013).

The relative permittivity of most of the organic solvent is less than water but formamide is more polar than water and its relative permittivity is higher than water (Moya *et al*., 2007). As alcohol changes, properties of water in alcohol-water mixed solvent i.e. alcohol lowers the relative permittivity of water (Onori and Santucci, 1992). When methanol is added in water, the relative permittivity of the medium decreases and the medium becomes more hydrophobic due to which the driving force for micellization decreases (Ali *et al*., 2014).

There was only one study of density and partial molar volume of SDS in alcohol-water mixed solvent media (Bhattarai *et al*., 2011).The density of the solution of SDS increased with increase in the concentration of SDS and decreases with increase in temperature in all volume fractions of methanol (Bhattarai *et al*., 2011). Partial molar volume at finite concentration was calculated with the help of literature (De Lisi *et al*., 1990; Wandrey *et al*., 1999) and found the partial molar volume of SDS was almost constant at the fixed temperature. However, by adding methanol to change the solvent composition partial molar volumes were found to decrease, indicating there was the presence of strong solute-solvent interactions. Temperature effect showed that partial molar volume increased with increment in temperature (Bhattarai *et al*., 2011).

The mixtures of cationic and anionic surfactants exhibit the largest synergistic effects such as the decrease in cmc and surface tension (Menger and Shi, 2009). The review on catanionic systems between 1943 and 1996 was done by Khan and Marques, 1997 and they noticed that most of the mixed cationic-anionic surfactant systems, commonly known as catanionic systems, precipitate at equimolar concentrations at very high water content. At non-equimolar concentration, the mixture forms micelles with different sizes and shapes, closed bilayer vesicles and dilute lamellar phases. The formation of aggregates and their transformation are rationalized in terms of interaction forces and surfactant geometry. These features were also illustrated by Tomasic *et al*., 1999 on the mixed system of cetyltrimethylammonium bromide-sodiumdodecyl sulphate. The precipitation occurred while mixing the equimolar amount of cationic (cetyltrimethyl ammonium bromide) and anionic (sodiumdodecyl sulphate) surfactants. Therefore, while making the solution of surfactants' mixture, it was found to use the excess amount of sodiumdodecyl sulphate in comparison to cetyltrimethyl ammonium bromide because, at a very high excess of one of the surfactants, the systems became clear due to mixed micelle formation (Tomasic, *et.al*, 1999). To explain solution properties of the binary mixture of CTAB and SDS there is very little work in literature (Tomasic *et al*, 1999). As a surfactant mixed surfactant also undergoes abrupt changes in the physicochemical behavior (Haque *et al*., 1996). In the mixture of cationic and anionic surfactants, the oppositely charged surfactant can behave as counterion to each other and reduce the repulsive force (Li and Liu, 1994; Sohrabi *et al*., 2008; Tondre and Caillet, 2001). In the mixture of sodiumdodecyl sulphate and cetyltrimethylammonium bromide,the concentration of sodiumdodecyl sulphate was taken more because sodiumdodecyl sulphate interacts with cetyltrimethylammonium bromide hydrophobically and favor micellization because anionic surfactants were known for having stronger hydrophobic interactions as compared with cationic surfactants (Bakshi,1999a; Bakshi,1999b). Mixed micelles are used by cosmetic industries in low concentration to keep away from skin irritation (Gracia *et al*., 1992; Robinson *et al*., 2005). In the field of medicine mixed micelle is very important. Mixed micelle increases the absorption of different drugs in the human body (Bhattarai *et al*., 2013).

In presence of CTAB, the density of SDS increased and decreased with increase in temperature (Chauhan *et al*., 2010; Bhattarai *et al*., 2013) and apparent molar volume of SDS in the presence of CTAB was found to increase with the increase in temperature over the entire concentration range. At a particular temperature, the apparent molar volumes were found almost same in the given concentration range (Bhattarai *et al.*, 2013).

The solubility of inorganic salts in water as the solubility of NaBr, NaCl, and KBr in SDS-water mixture increases with increase in temperature. The solubility of such salts in SDS-water mixture was relatively much lower than in pure water (Zhou and Hou, 2011).

The fact about the formation of micelles from ionic surfactants is that hydrophobic driving force competes with the electrostatic repulsion arising from ionic heads (Kronberg, *et al*. 1995). One of the fundamental properties of surfactants is their self-association into organized molecular structures called micelles (Khan *et al.,* 2008). The micelle is the simplest class of association colloid. The particular value of concentration where the association process starts is called critical micelle concentration and it is represented by cmc (Dominguez *et al*., 1997).The concentration of surfactant above which a surfactant aggregates into micelles is the cmc (Ruckenstein and Nagarajan, 1975). By using du Nouy ring tensiometer, micellisation properties of SDS was studied and showed (Azum *et al*, 2016; Rosen, 2004; Rub *et al*, 2016a; Ruckenstein and Nagarajan,1975), the effect of temperature on cmc. The cmc decreased to a minimum value at 21.48℃ and then increased giving U shaped curve on plotting cmc versus temperature (Noudeh et al., 2007b). In scientific literature, a term micelle was introduced by a Swiss botanist Karl Wilhelm von Nageli in 1858. It was derived from Latin word mica whose meaning is crumb (a small particle of bread) (Morris, 1986). The cmc of SDS increases with increase in methanol. This micellization can be explained on the basis of hydrophobic interaction (Chandler, 2005)between tails and electrostatic repulsion between ionic heads (Ghosh and Baghel, 2008). Hydrophobic interaction depends on the relative permittivity of the medium. Methanol has lower relative permittivity than of water and when methanol is added to water, the relative permittivity of the medium decreases (Yilmaz, 2002) due to which hydrophobic interaction becomes less, that ultimately increase the cmc.

Above the cmc, monomers, and micelles exist in dynamic equilibrium. The cmc is an indicator of the strength at which detergent binds to protein i.e. low value indicates strong binding and the high value indicates weak binding. According to thumb rule, the cmc of the amphiphilic substance decreases to about 10 times by increasing hydrophobic chain length by two methylene group having the same head group (Broecker and Keller, 2013).

The cmc depends on many variables i.e temperature, pressure, the chain length of hydrocarbon, the presence of various kinds of additives (Shinoda and Nagakawa, 1963; Tanaka *et al*., 1973). The cmc decreases with increase in hydrocarbon chain length (Mahmood and Al-Koofee, 2013) and with the addition of electrolyte (Baloch *et al.*, 2002). It increases with increase in temperature, the decrease in charge density of the counter ion. The incorporation of additive into an aggregate of an amphiphiles will affect its physicochemical properties such as the degree of dissociation, reaction rates and cloud or phase separation (Azum, *et al*, 2017a; Azum, *et al*, 2016; Azum, *et al*, 2014; Rub *et al*, 2016b; Schreier *et al*, 2000). Determinations of micellization parameters like aggregation number, critical micelle concentration, etc are helpful to understand micellization characteristics of a surfactant (Chakraborty *et al*., 2011). The value of cmc can be determined by the study of different physicochemical properties of the surfactant solution like osmotic pressure, electrical conductance, surface tension, viscosity, density, etc. The solution properties of amphiphiles were sensitive to the presence of additives. The values of cmc were found to depend on the type and nature of additives (Kabir-ud-Din *et al*., 2011). The cmc of ionic surfactant increases with increase in temperature in different organic solvents having the different relative permittivity and intermolecular H-bonding capacity, like N-methyl acetamide (NMA), Formamide (FA), etc as well as in water (Singh and Swarup 1978). The cmc of SDS in N-methyl acetamide and N- methyl formamide is less than in water but in some other solvents like dimethyl sulfoxide, formamide, etc have higher cmc than in water at the same temperature (Singh and Swarup 1978). Singh *et al* studied the cmc of SDS in nonpolar solvents by conductance measurements and calculated standard enthalpy of micellisation and standard entropy of micellisation (Singh *et al*., 1980).On study of micellisation of SDS in dimethylsulfoxide (DMSO) in the presence of lauric acid (LA) at 298.15-313.15 K showed that cmc increases with increase in temperature. The value of cmc of SDS in mixture of DMSO and LA was less than in pure water or in pure DMSO. The value of $\Delta G_{\mathrm{m}}^{\circ}$ and $\Delta H_{\mathrm{m}}^{\circ}$ of SDS in the mixture of DMSO and LA was more negative than in pure water or in pure DMSO (Ali *et al*., 2014).

On the study of effects of six different alcohols hexanol, octanol, decanol, dodecanol, tetradecanol, and hexadecanol found that the micelles were changed by the alcohol molecules into cylindrical and bilayer micelles as a function of the alcohol/SDS mass ratio (Mendez-Bermudez and Dominguez, 2016). The study of micellisation of SDS in n-alcohol-water mixtures at different temperatures indicates that with some exception cmc and degree of dissociation increased with increase in temperature and degree of dissociation also increased with increased in percentage of alcohol but cmc was not in regular order it means in ethanol the cmc was increased with increase in amount of alcohol but in propanol and butanol cmc initially increased with increase in temperature but was decreased at relatively higher concentration of alcohols (Rafati and Safarpour, 2006).

The micellar properties of SDS in the aqueous mixture of ethylene glycol (EG) were determined using different techniques like conductivity, density, surface tension, viscosity, etc measurement. The value of the degree of dissociation (α) was calculated. With the help of cmc, Gibb’s free energy of micellisation of SDS in water and in mixed solvent media was calculated (Gracie *et al*., 1996).

The study of the micellisation of SDS in CTAB in water and in methanol-water mixed solvent media by conductometry showed cmc and degree of dissociation (α) increased with increased in temperature and also increased in methanol-water mixed solvent media and it was calculated Gibb’s free energy of micellisation, enthalpy of micellisation and entropy of micellisation (Bhattarai, 2015).

Addition of alcohol or any other solvent which acts as water structure breaker decreased the hydrophobic effect, resulting in an increase in the cmc in ionic surfactants (Gunaseelan and Ismail, 2003). In aqueous solution hydrocarbon tails formed the core of micelle and polar head groups surrounded the micelle and in non aqueous media polar heads formed core of micelle and non polar tail groups surrounded the micelle (Tyowua *et al*., 2012).

The cmc of ionic surfactants including SDS influenced on the addition of ethanol. When ethanol was in small concentration the cmc decreased but the addition of more amount of ethanol cmc increased after certain concentration (Huang *et al*., 1999).

The effect due to the addition of ethanol on the micellization of SDS was investigated by using potentiometric and pulsed field gradient–NMR spectroscopic techniques.Potentiometry study showed that the cmc of SDS to a minimum value at around 10% ethanol. The minimum value of cmc at 10% ethanol was also in the literature (Gracie *et al*., 1996). The viscosity of the solvent mixture remains almost constant on the addition of ethanol of different percent (v/v) (Javadian, 2008). The aggregation behavior of sodiumdodecyl sulfate studied in 1,4-Dioxane−water and methanol−water media up to 50 percent by volume using calorimetry, conductometry, tensiometry, viscometry, NMR and DLS method and showed that cmc as well as β increased with addition of methanol and further increased with increment in the amount of methanol (Pan *et al*., 2012)

The cmc of SDS decreased with the addition of sodium acetate and sodium propionate in aqueous solution as inorganic salts like NaCl. Above the certain concentration of acetate and propionate salt, cmc increased with increase in the concentration of salts but such decrease in cmc with the increase in the concentration of added sodium chloride is continuous. It showed that co-ions like acetate, propionate, etc. perform differently than the other inorganic co-ions (Paul *et al*., 1998).

The conductance of ionic surfactants depends on nature of ions formed after dissociation of surfactant, nature of the solvent used, temperature, the presence of additives like salts, etc. The electrical conductivity of a pure surfactant solution is due to the ionic conductivities of monomer ion, counterion, and ionic micelle (Paul, *et al*., 1998). The conductivity was determined by plotting specific conductivity against concentration (Dev and Ismail, 2001; Dev, *et al*., 2004; Evans, 1956; Goddard and Benson, 1957). The specific conductivities of surfactants depend on total surfactant concentration and with the temperature. The specific conductivity sharply increases in the pre-micellar region with the increase in surfactant concentration but which is somewhat reduced after certain concentration which indicates the critical micelle concentration (Shah, *et al*., 2001). All ionic surfactants undergo substantial slope change in the plot of specific conductance versus concentration. The cmc was determined by finding the break at a fixed concentration value of such plot (Shanks and Franses, 1992). The ratio of the slope of conductivity (K) versus concentration (c) curve above and below the cmc is called counterion binding parameter (*ß*).

Perez-Rodríguez*et al* at 1998 measured the cmc of SDS at 298.15 K by conductivity measurement using three methods and by measuring relative permittivity. The values of cmc obtained by them in these three methods were almost same. They were in conductivity measurement (Williams method: 8.28 mM; Phillips proposed method: 8.22 mM and Phillips classical method: 8.21 mM) but found to be low 7.91 mM on measuring relative permittivity method. The aqueous solution of sodium salicylate (NaSa) did not affect the cmc of SDS when the concentration of NaSa was up to 0.03 mol kg^{-1} but above this concentration, salicylate affected the cmc (Umlong and Ismail, 2006).

The cmc of SDS decreased with increase in 1-butanol content and passed through a minimum at approximately 0.5 mol kg^{-1} of 1-butanol (Gunaseelan and Ismail, 2003). Almgren *et al* at 1985 investigated the effect of formamide and other solvents including dimethylsulfoxide and dimethyl acetamide on the micelle formation of SDS, and reduction of both cmc and mean aggregation number SDS micelle upon the addition of formamide. Rodrıguez *et al*. at 2008, studied effect of addition of polar organic solvents on micellisation and calculated the cmc, micellardissociation degrees and Gibbs energy of micellization for SDS, with other some surfactants (CTAB, Triton X-100, TTAB, DTAB) in water-organic solvent (formamide, ethylene glycol, glycerol, dimethyl sulfoxide , N-methyl formamide, N-methyl acetamide).

The cmc of SDS in aqueous solution increased with increase in temperature and the value of cmc at 293.15, 298.15, 303.15, 308.15 and 313.15 K were 7.94, 8.05, 8.50, 8.97, 9.57 mM respectively (Shah *et al*., 2001). The cmc of SDS determined by conductance measurement in acetamide melt at 89°C was 0.017 mol kg^{-1} (Dev *et al.*, 2004).

On the study of thermodynamic parameters of SDS in n-alcohol-water mixture found that the negative value of $\Delta G_{\mathrm{m}}^{\circ}$ increased with increased in temperature at the fixed composition of mixture but decreased with increased in volume fractions of alcohol at the fixed temperature. The values of $\Delta S_{\mathrm{m}}^{\circ}$ increased with increase in temperature at the fixed percentage of the mixture. The $\Delta S_{\mathrm{m}}^{\circ}$ did not show regular behavior with the increase in the percentage of different alcohols, it means in ethanol $\Delta S_{\mathrm{m}}^{\circ}$decreased with the increase of alcohol but in case of propanol and butanol $\Delta S_{\mathrm{m}}^{\circ}$ mostly increased with increase in the percentage of alcohol (Rafati and Safarpour, 2006).

The study of effect micellisation of counterion on SDS at 30°C showed that the cmc decreased with the addition of NaCl, negative values of $\Delta G_{\mathrm{m}}^{\circ}$ decreased in presence of NaCl. With the increase in the percentage of NaCl negative values of both $\Delta G_{\mathrm{m}}^{\circ}$ and $\Delta H_{\mathrm{m}}^{\circ}$ increased. The values of $\Delta S_{\mathrm{m}}^{\circ}$ did not show regular order that is it slowly increased up to the presence of 25mM NaCl and decreased up to 100mM and again increased up to 800 mM studied concentration (Naskar*et al.*, 2013).

The experimental value of cmc of SDS in aqueous solution was 8.1×10^{-3} M dm^{-3} (Mihali *et al.*, 2008). Electrolyte significantly affects aggregation of ionic surfactants, which mainly depends on the interaction of counterions (Umolong and Ismail, 2006). Counterions have sufficient effect but co-ions have the negligible effect on micellisation. In case of counterions with the same charge thecritical micelle concentration increase with increasing hydrated radius of cations. The hydrated radius of alkali metal ions were in the order Li^+ (2.31)> Na^+ (1.78) > K^+ (1.22) > Cs^+ (1.16) and cmc of SDS was in the order Li^+ (0.00796 M)> Na^+ (0.00762 M) > K^+ (0.00733) > Cs^+ (0.00692) (Goddard *et al.*, 1953). Corrin and Harkins at 1947 measured the cmc of SDS in pure water and in presence of NaCl of concentration from 2.047×10^{-3} to 3.540×10^{-1} M and found the lower value of cmc with the increase in the concentration of NaCl under similar other condition.

Singh *et al.*, at 1979 studied the effect of electrolytes on the micellization of ionic surfactants in 4% butanol and concluded smaller and highly solvated ions were more effective in reducing the cmc than the larger and less solvated ions. They stated that the tendency of micelle formation in the presence of different electrolytes follow the order LiC1 > NaCI > KCI > CsCl for SDS and KC1 > KBr > KI for CTAB. They have also calculated the change in free energy, change in enthalpy and change in entropy. The cmc of SDS decreased with the addition of salt. The decrease in cmc with the addition of salt was found to increase with the increase in the concentration of some salts like NaCl, KCl, NH_4ClO_4, $Mg(ClO_4)_2$, etc (Corrin and Harkins, 1947; Dutkiewicz and Jakubowska, 2002). The effect on cmc by addition of cation was more than that of anion. On addition of Na^+ and K^+ value of cmc decreased as $Na^+ < K^+$. The decrease in cmc on addition of KCl was more than in addition of NaCl (Baloch, *et al.*, 2002; Dutkiewicz and Jakubowska, 2002). The order of decrease of cmc of SDS in some electrolytes was reported $Na^+ < NH_4^+ < K^+ < Mg^{2+}$ (Dutkiewicz and Jakubowska, 2002).

Umlong and Ismail at 2007 studied the micellisation behavior of SDS in presence of different electrolytes and concluded the report given by Paul *et al.*, at 1998 that was co-ions like acetate, propionate and butyrate did not have any effect on the micellisation of SDS although butyrate ion, showed the effect on the adsorption and aggregation number of SDS. It showed the co-ion up to four carbon atoms does not affect the cmc of SDS. More researchers were required to confirm the minimum number of carbon atoms necessary in the co-ion for showing effect on the cmc of SDS.In most of the cases cmc of surfactant decreased on addition of electrolyte (Kontogeorgis and Kiil, 2016) but in some systems, the cmc of charged surfactant increased in the presence of an electrolyte with a common ion (Letellier, *et al*., 2008). On investigation of effect of $NaClO_4$, $KClO_4$, $LiClO_4$, NH_4ClO_4 and $Mg(ClO_4)_2$ on the micellization parameters of SDS, it was found that the properties are mainly affected by cation. The decrease in cmc by cation was found maximum in case of Mg^{2+} and minimum in case of Li^+. The order of effect of studied monovalent salt's cation for decrease in micelle of SDS was $Li^+ < Na^+ < NH_4{}^+ < K^+$(Jakubowska, 2010). Kabir-ud-Din et al at 2011 studied micellization of amitriptyline hydrochloride (AMT) which is an antidepressant drug, in presence of non-electrolytes (urea/thiourea) and inorganic salts at different temperatures using conductivity and dye solubilization methods. Using cmc values obtained they had calculated thermodynamic parameters and discussed the results on the basis of the nature of additives. The cmc decreased with addition of inorganic salts and the order of decrease in cmc was found LiCl < NaF < NaCl < KCl < NaBr. The cmc increased in presence of urea/thiourea and the order was urea < thiourea (Kabir-ud-Din, *et al*., 2011). The cmc of dodecyl sulphate in presence of alkali metal ion at 25℃ decreased with decrease in hydration radius of hydrated ion. The value of cmc of dodecyl sulphate in the presence of alkali metal ion was $Li^+ > Na^+ > K^+ > Cs^+$.

The shape of micelle of SDS and other surfactants are generally spherical but, when spherical micelles grow they became either disc-like or cylindrical, when the aggregation number reaches a certain stage (Tyowua *et al*., 2012), in presence of high concentration of electrolyte, the micelles of hexadecyltrimethylammonium bromide were rod-like (Kushner *et al.*, 1952). Usually, ionic amphiphiles formed small nearly spherical micelles at low ionic strength. Increases of concentration of counter ions, the aggregation number increased up to 20 folds and the micelle undergo a sphere to rod shape transition (Motin *et al.*, 2012). The study of DMSO affected on the micellisation of SDS in dilute aqueous solution of NaBr showed that cmc increased with increase in percentage of DMSO and increased in temperature. In presence of dilute NaBr, the cmc decreased when percentage of DMSO in solvent was lower. When percentage of DMSO increased in solvent, the dilute solution of NaBr did not affect cmc but in presence of more concentrate NaBr solution, the cmc of SDS decreased in the mixed solvent and further decreased with increased in concentration of NaBr (Chauhan *et al.*, 2003).

The micellar properties of SDS in NaCl from butanol to hexanol studied by small angle scattering (SANS), dynamic light scattering (DLS) and viscosity measurement. Addition of butanol leads to a decrease in micellar size. Moreover, in aqueous solution of SDS this formed the spherical micelle. Addition of neutral salt and alcohol affected the micellar structure (Forland *et al.*, 1994).

The $\Delta G_{\mathrm{m}}^{\circ}$ value calculated by using conductance measurement was negative for all systems. However,$\Delta H_{\mathrm{m}}^{\circ}$ for pure drug and drug-additive systems was negative at low temperature and positive at high temperature. The$\Delta S_{\mathrm{m}}^{\circ}$ value was positive at T = 308K (Kabir-ud-Din, *et al.*, 2011). It was seen that with the increase in temperature $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ values of SDS become less negative and hence indicate the less spontaneity of micellization. This fact can be known to protest of the micelle due to thermal forces at higher temperature (Ali *et al.*, 2014).

Gracie et al studied thermodynamic properties of SDS in different ethanol-water mixtures and showed that cmc and negative values of ΔH° increased but ΔS° decreased with increased in percentage of glycerol (Gracie *et al.*, 1996). The study of $\Gamma_{\max}$, $A_{\min}$,$\Delta G_{\mathrm{m}}^{\circ}$, $\Delta H_{\mathrm{m}}^{\circ}$, $\Delta S_{\mathrm{m}}^{\circ}$,$\Delta G_{\mathrm{ad}}^{\circ}$, of SDS in methanol-water mixed solvent at 303 K showed that values of $\Gamma_{\max}$, $\Delta G_{\mathrm{m}}^{\circ}$, $\Delta S_{\mathrm{m}}^{\circ}$ and $\Delta G_{\mathrm{ad}}^{\circ}$ were decreased $A_{\min}$, and $\Delta H_{\mathrm{m}}^{\circ}$ were increased with increased in percentage of methanol in the mixture (Pan et al., 2012).

The cmc of SDS in water and in presence of NaCl at different temperature were determined by Chatterjee et al. and calculated$\Delta G_{\mathrm{m}}^{\circ}$, $\Delta H_{\mathrm{m}}^{\circ}$, $\Delta S_{\mathrm{m}}^{\circ}$ and $\Delta Cp_{\mathrm{m}}^{\circ}$. The cmc was decreased in presence of NaCl and increased with increase in temperature. The negative value of $\Delta G_{\mathrm{m}}^{\circ}$increased with increase in temperature. The values of $\Delta H_{\mathrm{m}}^{\circ}$ were positive as well as negative. The value of $\Delta S_{\mathrm{m}}^{\circ}$were positive and decreased with increase in temperature.Moreover, the values of $\Delta Cp_{\mathrm{m}}^{\circ}$decreased with increase in temperature (Chatterjee *et al.*, 2001). Thermodynamic properties as standard Gibbs free energy of micellization, the standard entropy of micellization, the standard enthalpy of micellization, and the standard free energy of transfer were calculated (Perger and Bester-Rogac, 2007). $\Delta G_{\mathrm{m}}^{\circ}$ with Richard's Parameter (Chandler *et al*., 2005), The Hildenbrand parameter's (Ghosh and Baghel, 2008; Yilmaz, 2002; Marcus, 1985) and the Gordon Parameter's (Sjoeberg *et al.*, 1990) have been correlated. Thermodynamic properties$\Delta G_{\mathrm{m}}^{\circ}$, $\Delta H_{\mathrm{m}}^{\circ}$ and $\Delta S_{\mathrm{m}}^{\circ}$ were also calculated in ethanol-water mixture conductometrically (Onori and Santucci,1992). The study of degree of dissociation (α), cmc and $\Delta G_{\mathrm{m}}^{\circ}$ of SDS in formamide showed both α and cmc were higher in water-formamide mixture than in pure water and both increased with increase in percentage weight of formamide. The negative value $\Delta G_{\mathrm{m}}^{\circ}$was lower in mixed solvent than in pure water and further decreased with increase in percentage weight (Moya *et al*., 2007).

In presence of NaBr, $\Delta G_{\mathrm{m}}^{\circ}$ and $\Delta H_{\mathrm{m}}^{\circ}$ of SDS in aqueous solution decreased and such decrease was regular with increase in concentration of NaBr. The value of $\Delta S_{\mathrm{m}}^{\circ}$ decreased in such condition. In water-DMSO mixed solvent effect of NaBr on $\Delta G_{\mathrm{m}}^{\circ}$, $\Delta H_{\mathrm{m}}^{\circ}$ and $\Delta S_{\mathrm{m}}^{\circ}$ of SDS was found comparatively less (Chauhan *et al*., 2003).

The solvophobic parameter, $S_{\mathrm{p},}$ was calculated by Gibbs energies of transfer (Ruiz *et al*., 2008). By using correlation method developed by Wang et al. (Fuoss and Kraus, 1933), S_{p} values of the mixed solvents was calculated. With increase in temperature of SDS solution in water $\Delta S_{\mathrm{m}}^{\circ}$ decreases, it implies that disordering of water molecules becomes less pronounced due to the destruction of the iceberg water structure around the alkyl group with increasing temperature (Kabir-ud-Din and Koya, 2010).The dependence of $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ on the bulk phase in aqueous binary mixtures qualitatively explained by solvophobic effect (Moya *et al*., 2007).

The study of effect of temperature and pHon aqueous solution of SDS showed that the surface tension changes very slightly with the change in pH in the same other condition but with increase in temperature the surface tension was decreased (de Castro, 1998). Some of the surfactants showed a gradual decrease in surface tension until the micelle forms (Das *et al*., 2013). For the study of surface tension of any surfactant, it should be highly pure, presence of traces of impurities significantly affect the surface tension (Mysels, 1986). The plot of surface tension versus logarithm of concentration of SDS obtained minimum due to presence of highly surface active dodecyl molecule (Lin *et al.*, 1999). The cmc of SDS was calculated with the help of plot of surface tension versus logarithm of concentration of SDS and found 8.10 mmol kg^{-1} (Bhattarai *et al.*, 2013). Due to the presence of a hydrophobic tail, surfactant molecules are adsorbed on the surface of a solvent, even at very low concentrations, resulting in the surface activity of surfactants. Typically, surfactants showed a gradual reduction in surface tension until the micelle forms (Holmberg *et al.*, 2002; Niraula *et al.*, 2017a). The presence of an organic solvent greatly affects the surface properties of surfactant solutions (Das *et al.*, 2013; Das *et al,* 2012; Zdziennicka, 2008).

The study of viscosity is very important to know the behavior of solute-solvent interaction (Tomas *et al.*, 2015). Investigation of the viscosity of a solution provides information about the interaction between the surfactant and mixed solvent media, which is applicable to many different fields of applications (Kumar and Rub, 2017; Singh, 2005). Studies of SDS using surface tension and viscosity measurements in methanol-water mixed solvent media are very few (Niraula *et al.*, 2014; Pan *et al.*,2012).Viscosity is an important measurement characteristic in the food, paint, polymer coating, and other industries where the flow is a critical product or use characteristic (Lane and Henderson, 2004). Temperature is a most important factor affecting the quality of a viscous substance. For petroleum products as their rate of viscosity change per unit temperature was significantly greater than other products. Thus a slight variation in temperature can have a very large effect on the viscosity of a fluid. This interaction is used to describe the properties of the microemulsion and liquid crystal with respect to the micellar solution of surfactant system (Lane and Henderson, 2004). Investigation of the viscosity of a solution provides information about the interaction between the surfactant and mixed solvent media, which is applicable to many different fields of applications (Shah *et al,* 2016).

On addition of ethanol to the aqueous solution of SDS, the viscosity of solvent was remained almost constant indicating that the addition of ethanol did not affect the structure of micellar but relative viscosity increased with increased in percentage of alcohol (Javadian, 2008).

The plot of relative viscosity of the aqueous solution of SDS containing pentanol and hexanol in presence of NaCl against molality of alcohol showed that the viscosity of SDS increased with increase in the amount of alcohol and the increase in viscosity further increased with increase in concentration of NaCl (Forland*et al.*, 1994). The study of the relative viscosity of SDS in 50%, 60% and 90% methanol-water mixture showed that the relative viscosity increased with increase in concentration of SDS and the viscosity is further increased with increased in percentage of methanol (Pan *et al.*, 2012).The viscosity of SDS in butanol-water increased with increase in concentration. The viscosity of SDS increased on addition of inorganic salts in SDS solution in the butanol-water. The value of viscosity of SDS in the butanol-water mixture in the presence and in absence of some salts is in the order without salt < presence of NaCl < presence of KCl< presence of CsCl (Singh and Swarup, 1979).

Study of surface properties of SDS in the aqueous mixture of ethanol glycol showed that values of Γ_{max} and π_{cmc} decreased with increased in temperature but values of A_{min} increased. The value of Γ_{max} and π_{cmc} decreased and values of A_{min} increased with increased in percentage of glycol in the mixture (Gracie *et al.*, 1996).

CHAPTER 3

3. MATERIALS AND METHODS

3.1 Preparation of Solvent

3.1.1 Preparation of Mixed Solvent at Different Temperatures

1000 ml of double distilled water, specific conductance less than 10^{-6}S $cm^{-1}$and about 500 ml methanol were taken in separate 1000 ml volumetric flasks. Both volumetric flasks were fixed in thermostat and heated to about 15 minutes. For the preparation of different volume fractions of mixed solvent required volume of water was taken out from the flask and the same volume of methanol was added with the help of two separate 25 ml pipettes. The mixture was left for 24 hours for homogeneous mixing. Amount of water taken out and methanol added for the preparation of different volume fractions of methanol are shown in Table 3.1.

Table 3.1 Preparation of mixed solvent

Volume fractions of methanol	Volume of water taken out from volumetric flask (ml)	Volume of methanol mixed with water (ml)
0.1	100	100
0.2	200	200
0.3	300	300
0.4	400	400

3.1.2 Preparation of 0.1M solution of SDS at 298.15, 308.15, 318.15 and 323.15 K

Sodiumdodecyl sulphate used in these investigations was purchased from Merck Specialties Private Limited, Mumbai, India. SDS was taken in a weighing bottle and kept for one hour in the oven at $60^{\circ}C$ by slight opening the lid for drying. The bottle was cooled to room temperature and 2.8828 g of SDS was transferred carefully in four 100ml volumetric flasks using 4 digits electric balance. About 25 ml of required solvent was added to the volumetric flask containing SDS and left to about 24 hours to dissolve by covering with the lid. After 24 hours when SDS has completely dissolved the flasks were heated for 15 minutes in water-bath at the required temperature and hot solvent of required temperature was added to the flask up to the mark.

3.1.3. Preparation of 0.1M Solution of Monovalent Salts (NaCl, NaBr, KCl and KBr) at 298.15, 308.15, 318.15 and 232.15 K

Salts (sodium bromide, potassium bromide, sodium chloride and potassium chloride) employed in these investigations were purchased from Ranbaxy Chemical Company, Mumbai, India**.**

Required salts in weighing bottles were kept in the oven at $60^\circ C$ in slightly opening the lid of weighing bottle for one hour for drying and let to cool up to room temperature by closing the lid after taking out from the oven.

0.51445 g, 0.2922 g, 0.3728 g and 0.5850 g of dry and cold NaBr, NaCl, KCl and KBr were taken in different 50 ml volumetric flasks. Each salt was dissolved in the required solvent at the required temperature and the volume was prepared up to mark.

3.1.4. Preparation of Solution of Sodiumdodecyl Sulphate–cetyltrimethylammonium bromide

Cetyltrimethylammonium bromide was purchased from Loba Chemical Private Limited India and it was recrystallised several times until no minimum in the surface tension-concentration plot was observed. The solution of SDS in the presence of CTAB was prepared in pure water and methanol-water mixed solvent media at 298.15, 308.15, 318.15 and 323.15 K. The densities of solutions were determined by the use of specific gravity bottle of about 25 cm^3 capacity. The sample solution was transfused into the specific gravity bottle by using a medical syringe. The specific gravity bottle was then tightly fixed in a thermostat at the experimental temperatures within ± 0.005 K. After thermal equilibrium was attained, the mass of the specific gravity bottle was measured with the electronic balance and the density was calculated.

3.2. Measurement of Density of a Solution at 298.15, 308.15, 318.15 and 323.15 K

The densities of the solutions were determined by using specific gravity bottle of about 25 ml capacity. The sample solution was taken into the specific gravity bottle by using the medical syringe. The specific gravity bottle was then tightly fixed in a thermostat at the experimental temperatures within the variation of ± 0.005 K. When thermal equilibrium was attained, the mass of the specific gravity bottle was measured with the electronic balance. The mass of solvent was also taken after heating the solvent till thermal equilibrium. For calculation of density equation (1.1) given above was used. In all the cases, the experiments were performed in three replicates.

3.3. Measurement of Conductance of a Solution at 298.15, 308.15, 318.15 and 323.15 K

The conductance of SDS was carried out on a Labtronics ISO 9001:2000 certified conductivity meters at a frequency of 2000 Hz using a dip-type cell with a cell constant of 1.15 cm^{-1} and having an uncertainty of 0.01%. The cell was calibrated using aqueous potassium chloride solution (Lind *et al*., 1959). The measurements were made in a water bath maintained at 298.15, 308.15, 318.15 and 323.15 K within ± 0.005 K. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. A correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium from those of the electrolyte solutions. In all cases, the experiments were performed in three replicates.

3.4. Measurement of Surface Tension of a Solution at 298.15, 308.15, 318.15 and 323.15 K

Surface tension of solution was calculated by pendant drop number (PDN) method by using the Mansingh Survismeter. Mansingh Survismeter is represented in **Figure 3.1**.Surface tension is generally represented by a Greek letter gamma (γ).

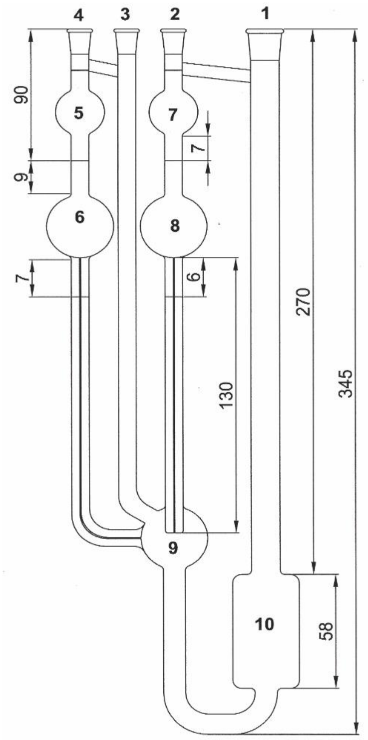


Figure 3.1: Mansingh Survismeter

In Mansingh Survismeter representations are 10: Reservoir 9: Carburetor 6 for viscous flow 5, 7: buffer 8: for dropwise flow Limbs nomenclature 9 to 3: for pressure 10 to 1: overhead pressure sockets: 1, 2, 3, 4 for blocking pressure 10 to 8 surface tension capillary 10 to 9 Hyphenating bend.

3.5. Measurement of Viscosity of a Solution at 298.15, 308.15, 318.15 and 323.15 K

Viscosities of solutions were calculated by using viscous flow time (VFT) method using the Mansingh Survismeter. In this method, the time flow for the given volume of solution and the same volume of solvent was taken with the help of digital stopwatch and the viscosity was calculated.

CHAPTER 4

4. RESULTS AND DISCUSSION

This chapter includes the important findings of the research and discusses it in different terms such as density, conductivity, surface tension viscosity measurements and calculation of partial molar volume, surface properties, viscometric properties, thermodynamic parameters, solvent parameters as well asthesolvophobic parameter.

4.1 Properties of Methanol-water Mixed Solvent Media

When methanol is mixed with water, the volume is reduced in measurable quantity. The decrease in volume may be due to the breaking of the iceberg of water. The relative permittivity of water decreases with the addition of methanol. The surface tension of water decreases but viscosity increases when methanol is added in water. Such unique properties of methanol drew the interest of the research.

4.2 Study of Density and Partial Molar Volume of Sodium Dodecyl Sulphate

The partial molar volume is a very useful method in illustrating the interactions occurring in solutions. Studies of partial molar volumes of surfactants in different organic compound-water solvent mixtures have been studied (Bhattarai *et al*., 2011).

The partial molar volume “V_B" is defined by the following equation;

$$V_{B} = \left(\frac{\partial v}{\partial n}\right)_{T,P} \quad \dots\dots\dots\dots\dots\dots \quad (4.1)$$

Here, ∂v represent the change in total volume and n as the number of moles. The unit of partial molar volume is cm^3 mol^{-1}. If there is concentration dependence, the partial molar volumes have to be extrapolated to concentration zero using one of the following two equations which calculate the apparent volume at the finite concentrations, C (Shah *et al*., 2014).

$$\mathrm{V} = \frac{1}{\rho_0} - \frac{1}{C}\left(\frac{\rho}{\rho_0} - 1\right) \quad \dots\dots\dots\dots\dots\dots \quad (4.2)$$

$$V_{\mathrm{B}} = \frac{M}{\rho_0} - \frac{10^3}{C}\left(\frac{\rho}{\rho_0} - 1\right) \quad \dots\dots\dots\dots\dots\dots \quad (4.3)$$

Here,

M is the molecular weight of the surfactant,ρ_0 is the density of the solvent and ρ is the density of the solution and C is the equivalent concentration in mol kg^{-1}.

In this study, the partial molar volume of SDS was determined at 298.15, 308.15, 318.15 and 323.15 K in pure water, 0.1, 0.2, 0.3 and 0.4 volume fractions of methanol. In order to calculate partial molar volumes, the solution densities were thoroughly measured for surfactant at the temperatures investigated in pure water and in methanol-water mixed solvent media.Properties of Methanol-Water Mixtures Containing 0.10, 0.20, 0.30 and 0.40 volume fraction of methanol at (298.15, 308.15, 318.15, and 323.15) K are given in Table 4.1

Table 4.1 Properties of methanol-mater mixtures Containing 0.10, 0.20, 0.30 and 0.40 volume fraction of methanol at (298.15, 308.15, 318.15, and 323.15) K (Bhattarai, 2010).

T/K	ρ_0/g.cm^{-3}	η_0/ mPa.s	D
	$\phi_1 = 0.1$		
298.15	0.98297	1.0844	75.09
308.15	0.97973	0.8665	71.57
318.15	0.97604	0.7017	68.18
323.15	0.97438	0.6375	66.45
	$\phi_1 = 0.2$		
298.15	0.96963	1.3106	71.61
308.15	0.96632	1.0217	68.14
318.15	0.96162	0.8075	64.80
323.15	0.95875	0.7300	63.15
	$\phi_1 = 0.3$		
298.15	0.95620	1.4712	67.65
308.15	0.95160	1.1418	64.25
318.15	0.94626	0.8957	60.99
323.15	0.94331	0.8052	59.41
	$\phi_1 = 0.4$		
298.15	0.93957	1.4475	63.53
308.15	0.93364	1.2034	60.34
318.15	0.93140	0.9309	57.18
323.15	0.92800	0.8288	55.62

Concentration, density and partial molar volume of sodium lauryl sulfate in pure water and methanol-water mixed solvent media at (298.15, 308.15, 318.15, and 323.15) K given in Table 4.2

Table 4.2. Concentration, density and partial molar volume of sodium lauryl sulfate in pure water and methanol-water mixed solvent media at (298.15, 308.15, 318.15, and 323.15) K.

C / mol.kg^{-1}	ρ/g.cm^{-3}	V_B /cm^3.mol^{-1}	C / mol.kg^{-1}	ρ/g.cm^{-3}	V_B/cm^3.mol^{-1}
	T = 298.15 K			T = 308.15 K	
		$\phi_1 = 0.00$			
0.11591	1.00171	249.08 ± 0.09	0.11635	0.99799	256.12 ± 0.11
0.09920	1.00107	248.79 ± 0.10	0.09957	0.99746	255.75 ± 0.13
0.08753	1.00063	248.44 ± 0.12	0.08785	0.99709	255.41 ± 0.14
0.07710	1.00024	247.99 ± 0.13	0.07737	0.99676	255.00 ± 0.16
0.05935	0.99950	248.16 ± 0.10	0.05955	0.99613	255.14 ± 0.21
0.04734	0.99903	247.70 ± 0.21	0.04749	0.99573	254.73 ± 0.27
0.04026	0.99874	247.63 ± 0.25	0.04040	0.99548	254.74 ± 0.19
0.03036	0.99833	247.60 ± 0.24	0.03046	0.99513	254.76 ± 0.25
		$\phi_1 = 0.10$			
0.12182	0.98867	245.78 ± 0.06	0.12232	0.98472	252.71 ± 0.08
0.10165	0.98773	245.74 ± 0.08	0.10205	0.98392	252.44 ± 0.09
0.08982	0.98721	245.35 ± 0.09	0.09017	0.98345	252.24 ± 0.11
0.07882	0.98670	245.23 ± 0.10	0.07912	0.98300	252.16 ± 0.12
0.06113	0.98588	244.95 ± 0.17	0.06135	0.98229	251.76 ± 0.15
0.04896	0.98529	245.17 ± 0.21	0.04914	0.98177	251.97 ± 0.19
0.04097	0.98492	244.96 ± 0.25	0.04112	0.98144	251.90 ± 0.25
0.03183	0.98449	244.80 ± 0.22	0.03194	0.98106	251.84 ± 0.22
		$\phi_1 = 0.20$			
0.11801	0.97567	244.63 ± 0.04	0.11851	0.97169	251.54 ± 0.04
0.10281	0.97490	244.55 ± 0.05	0.10323	0.97100	251.52 ± 0.05

0.08996	0.97427	244.22 ± 0.05	0.09032	0.97045	251.11± 0.05
0.07774	0.97366	243.95 ± 0.06	0.07806	0.96990	250.97 ± 0.06
0.05984	0.97275	243.64 ± 0.04	0.06007	0.96910	250.54 ± 0.09
0.04751	0.97210	243.80 ± 0.10	0.04769	0.96853	250.48 ± 0.08
0.04175	0.97181	243.56 ± 0.11	0.04190	0.96827	250.27 ± 0.12
0.03148	0.97128	243.36 ± 0.13	0.03159	0.96778	250.60 ± 0.18
			$\phi_1 = 0.30$		
0.12371	0.96301	244.02 ± 0.08	0.12441	0.95778	250.85 ± 0.08
0.10533	0.96204	243.60 ± 0.10	0.10591	0.95688	250.66 ± 0.10
0.09186	0.96130	243.53 ± 0.11	0.09236	0.95624	250.25 ± 0.11
0.07991	0.96066	243.22 ± 0.13	0.08034	0.95565	250.07 ± 0.13
0.05970	0.95956	242.73 ± 0.17	0.06002	0.95463	250.00 ± 0.17
0.04925	0.95896	242.98 ± 0.21	0.04951	0.95410	249.99 ± 0.21
0.04340	0.95864	242.79 ± 0.11	0.04362	0.95380	250.05 ± 0.19
0.03298	0.95806	242.61 ± 0.10	0.03315	0.95329	249.47 ± 0.16
			$\phi_1 = 0.40$		
0.12398	0.94697	243.40 ± 0.09	0.12487	0.94045	250.46 ± 0.03
0.10717	0.94599	243.17 ± 0.10	0.10793	0.93955	250.23 ± 0.08
0.09392	0.94520	243.13 ± 0.11	0.09457	0.93883	250.10 ± 0.07
0.08130	0.94447	242.78 ± 0.13	0.08186	0.93817	249.61 ± 0.09
0.05846	0.94311	242.48 ± 0.18	0.05885	0.93692	249.18 ± 0.07
0.04902	0.94255	242.23 ± 0.22	0.04935	0.93638	249.41 ± 0.12
0.04081	0.94205	242.25 ± 0.26	0.04108	0.93593	249.17 ± 0.10
0.03216	0.94153	242.06 ± 0.17	0.03237	0.93545	248.99 ± 0.08

The densities for the sodiumdodecyl sulphate in pure water 0.1, 0.2, 0.3 and 0.4 volume fraction of methanol at 298.15, 308.15, 318.15 and 323.15 K are shown in **Figures 4.1** to **4.9** which show the variation of densities of the investigated solutions as a function of the surfactants concentration. From these **figures**, it indicated that the densities exhibit almost increase with increasing concentration within the concentration range investigated. It also indicates that the density decreases with increase in temperature and volume fractions of methanol in methanol-water mixed solvent media. However, the density of the system increased with the addition of surfactant. Such variations are also found in the literature (Bhattarai *et al.*, 2011;

Chauhan *et al*., 2010). The decrease in density values of surfactants with the increase in temperature is also observed (Chauhan *et al*., 2010). The effects of relative permittivity and temperature on the densityvalues are shown from **Figures 4.1** to **4.9**. The density values for each temperature are found to decrease with decreasing relative permittivity in going from 0.10 to 0.40 volume fractions of methanol.

The partial molar volumes for sodiumdodecyl sulphate in pure water and 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol at 298.15, 308.15, 318.15 and 323.15 K as the function of surfactant concentration areshown in **Figures 4.10** to **4.18**. From these **figures**, the partial molar volumes exhibit almost independent nature with increasing concentration,within the studied concentration range. Our partial molar volume data for pure water of sodiumdodecyl sulphate also match with Durchschlag and Zipper, 1994 work at 298.15 K. The partial molar volume values for each temperature are found to decrease with decreasing relative permittivity with the addition of methanol, whereas the partial molar volume is increased with increase in temperature.

It is found that the partial molar volume decreases with increase in methanol content. When methanol and water are mixed with each other, the evolution of heat takes place which is due to rupturing the H-bond between the water molecules. The hydrogen bonding and closer packing of the molecules by the attraction allow a larger number of molecules of the hydrated alcohol to fit into the same space, thus decreasing the overall volume (Bhattarai *et al*., 2011).

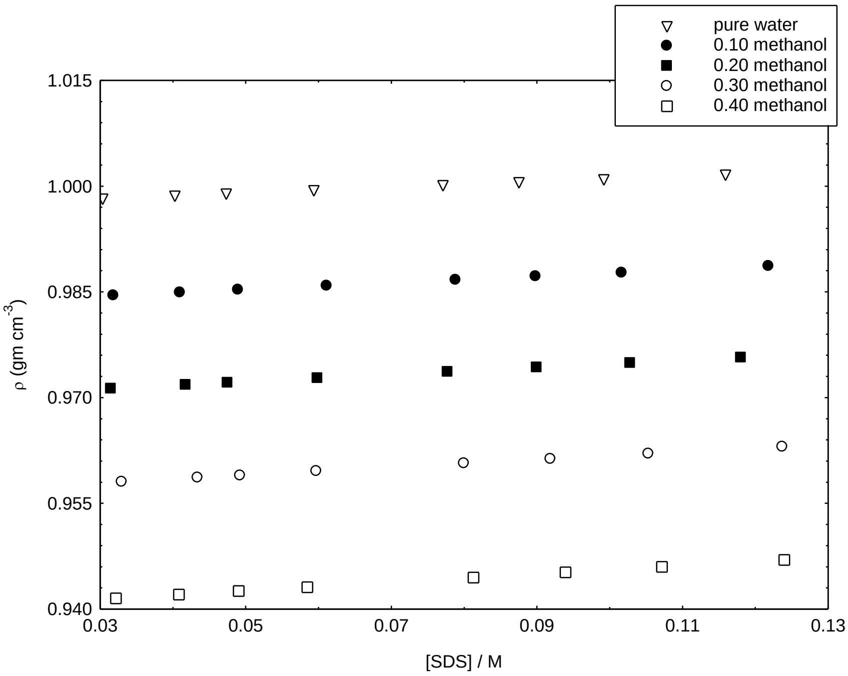


Figure 4.1: Concentration dependence of density for SDS at 298.15 K

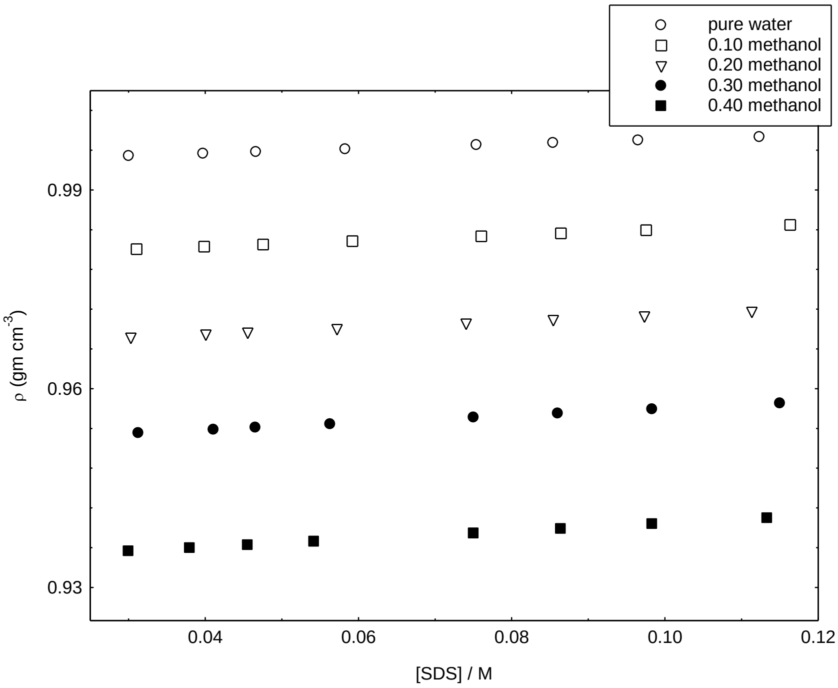


Figure 4.2: Concentration dependence of density for SDS at 308.15 K

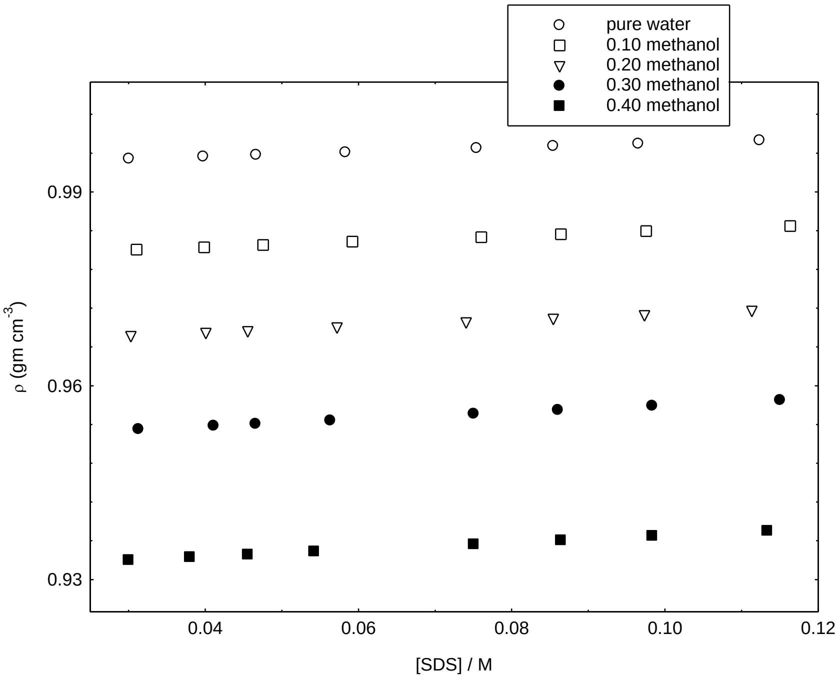


Figure 4.3: Concentration dependence of density for SDS at 318.15 K

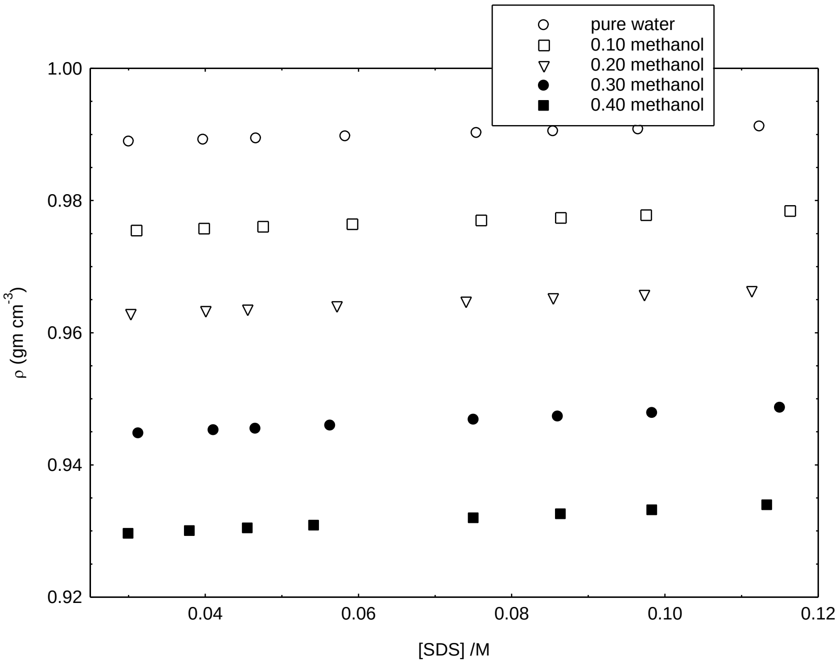


Figure 4.4: Concentration dependence of density for SDS at 323.15 K

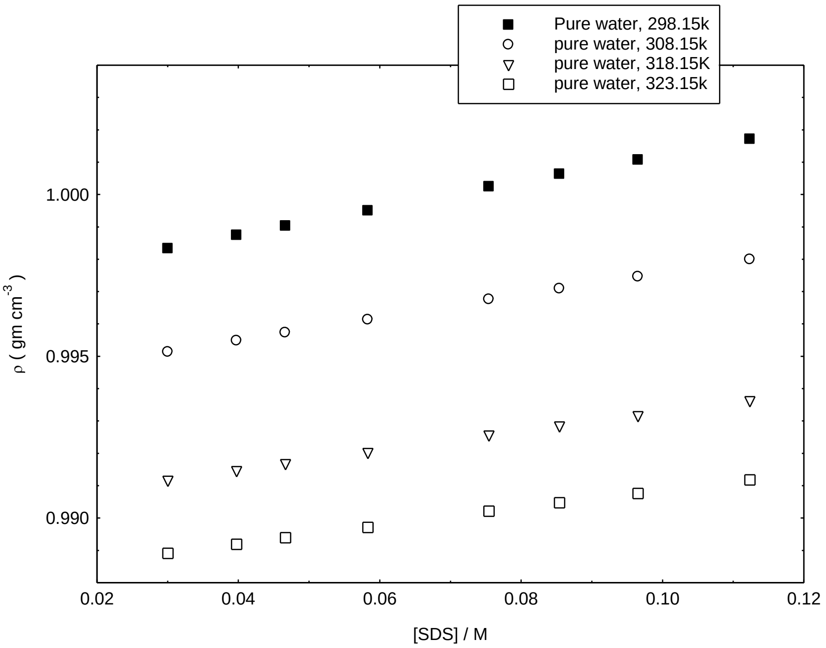


Figure 4.5: Concentration dependence of density for SDS at different temperatures in pure water

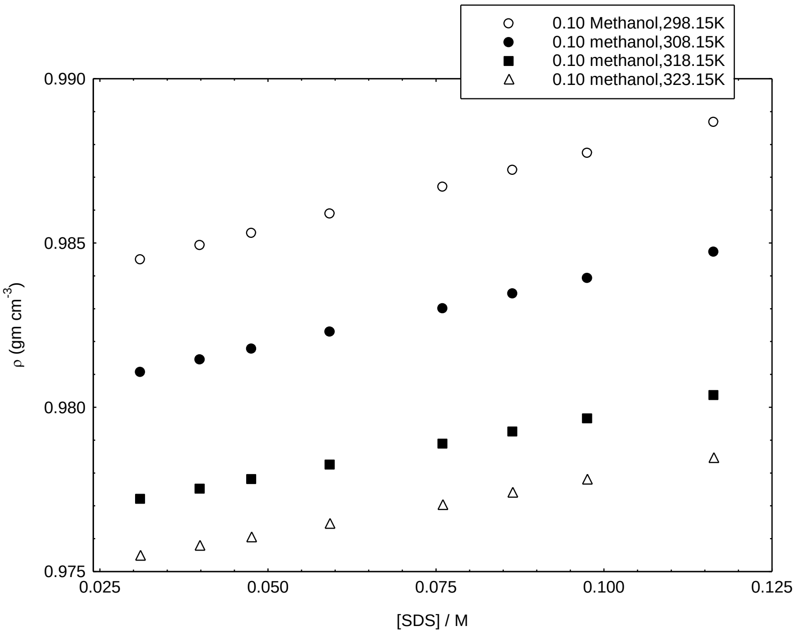


Figure 4.6: Concentration dependence of density for SDS at different temperatures in 0.10 volume fraction of methanol

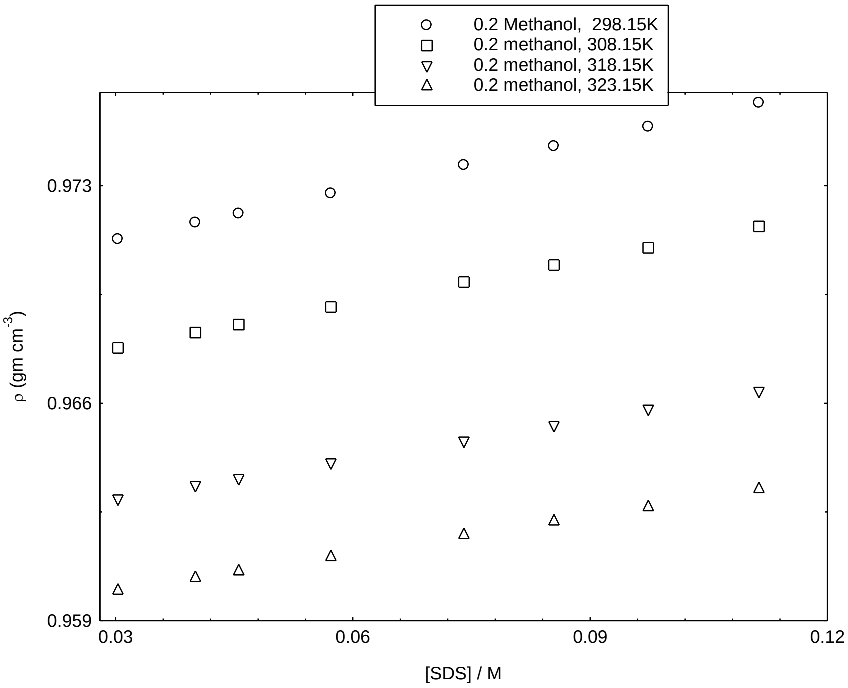


Figure 4.7: Concentration dependence of density for SDS at different temperatures in 0.20 volume fraction of methanol

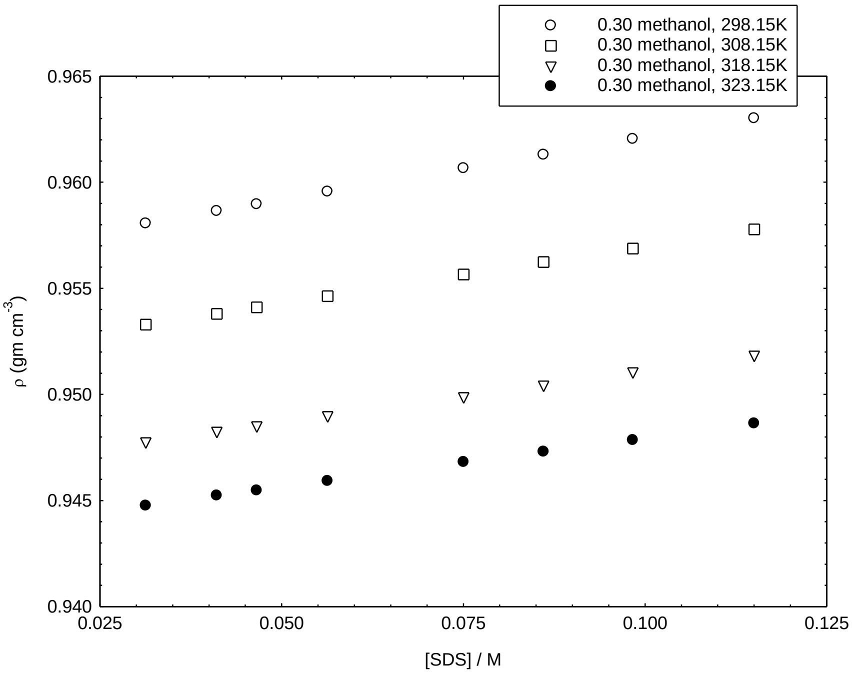


Figure 4.8: Concentration dependence of density for SDS at different temperatures in 0.30 volume fraction of methanol

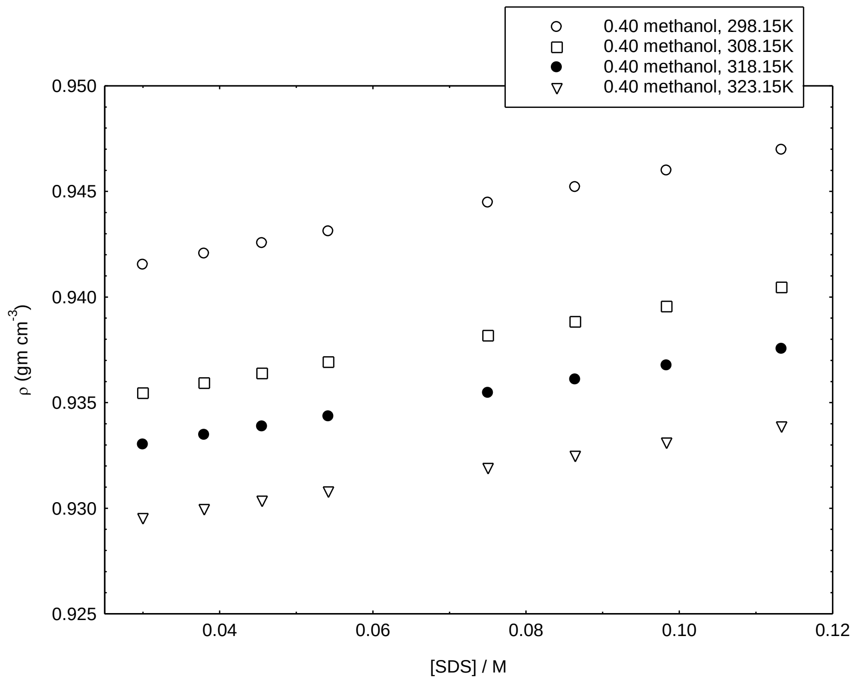


Figure 4.9: Concentration dependence of density for SDS at different temperatures in 0.40 volume fraction of methanol

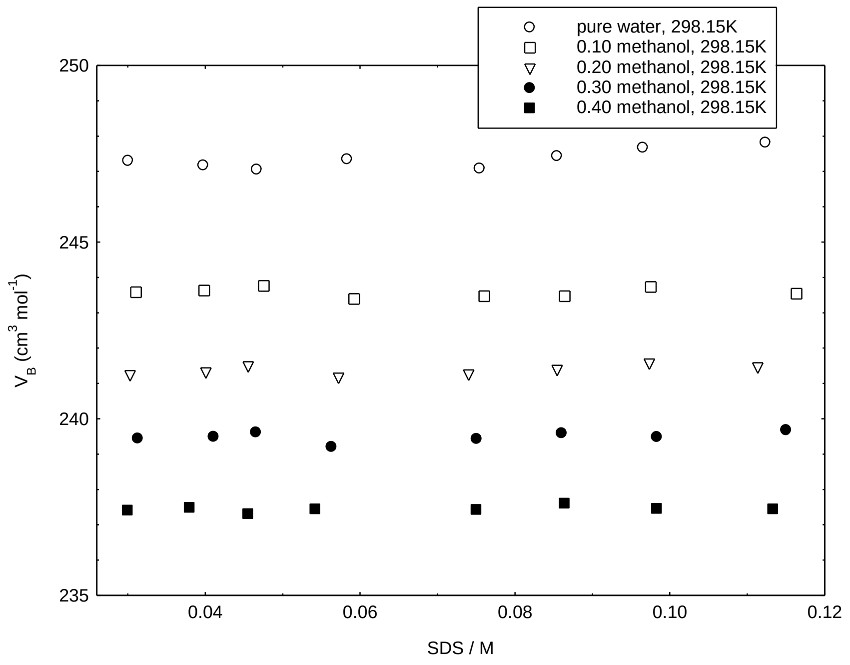


Figure 4.10: Concentration independence of partial molar volume for SDS at 298.15 K

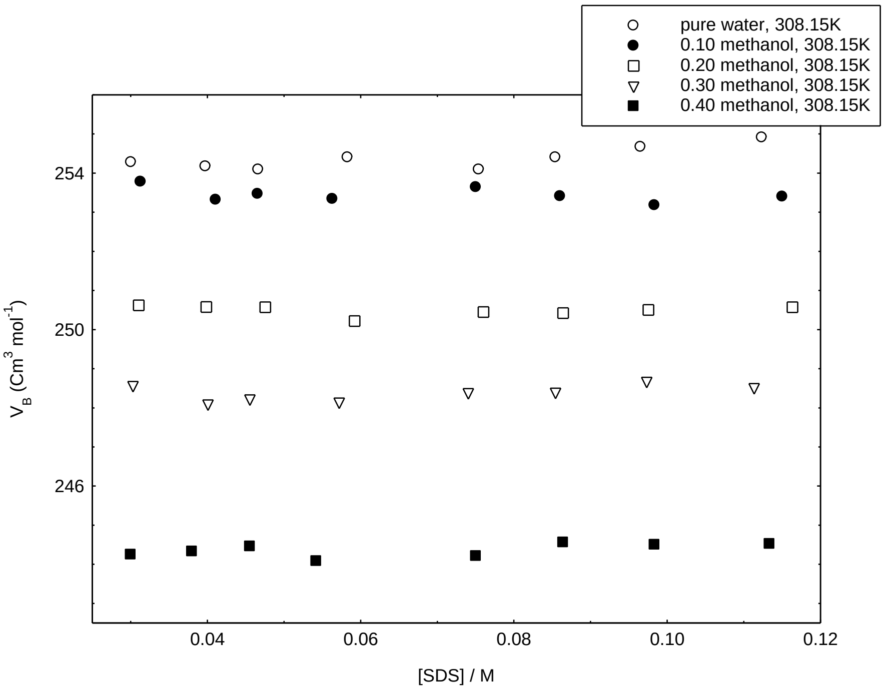


Figure 4.11: Concentration independence of partial molar volume for SDS at 308.15 K

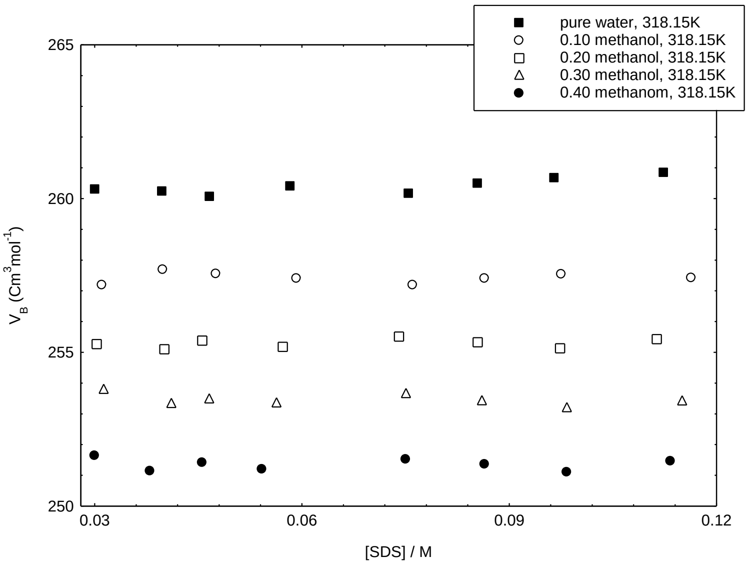


Figure 4.12: Concentration independence of partial molar volume for SDS at 318.15 K

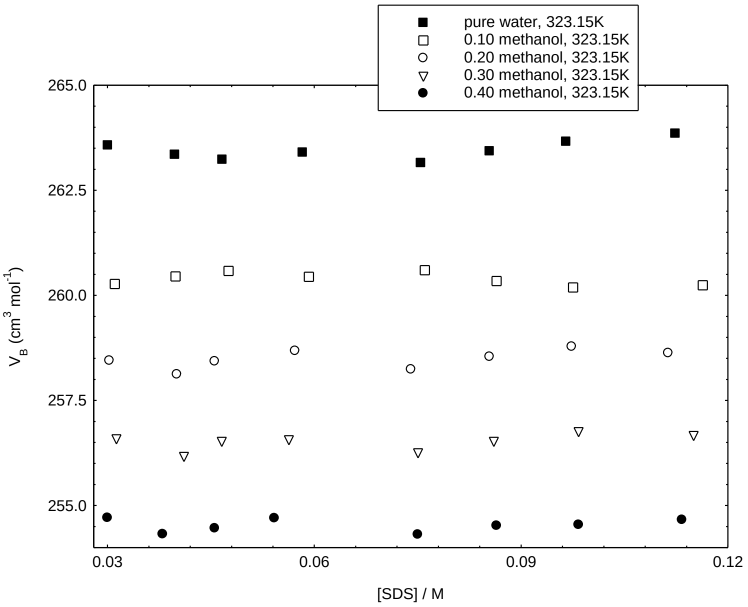


Figure 4.13: Concentration independence of partial molar volume for SDS at 323.15 K

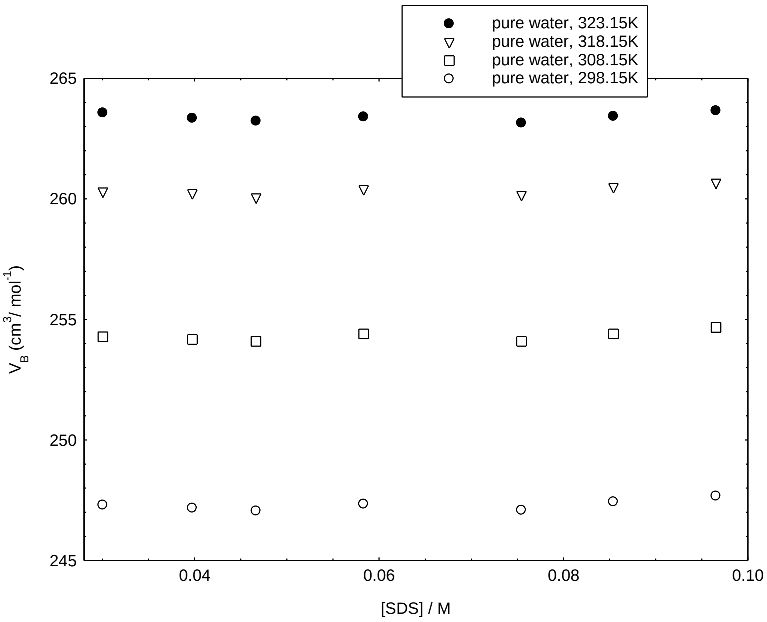


Figure 4.14: Concentration independence of partial molar volume for SDS at different temperature in pure water

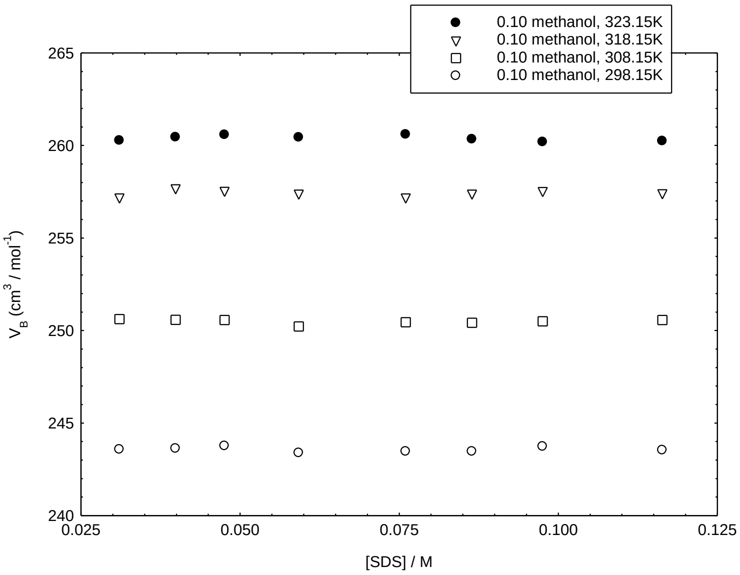


Figure 4.15: Concentration independence of partial molar volume for SDS at different temperature in 0.10 volume fraction of methanol

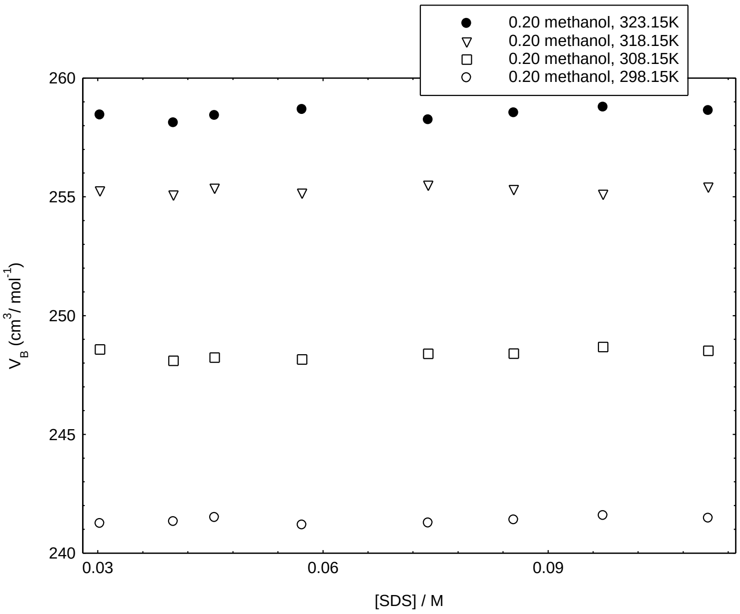


Figure 4.16: Concentration independence of partial molar volume for SDS at different temperature in 0.20 volume fraction of methanol

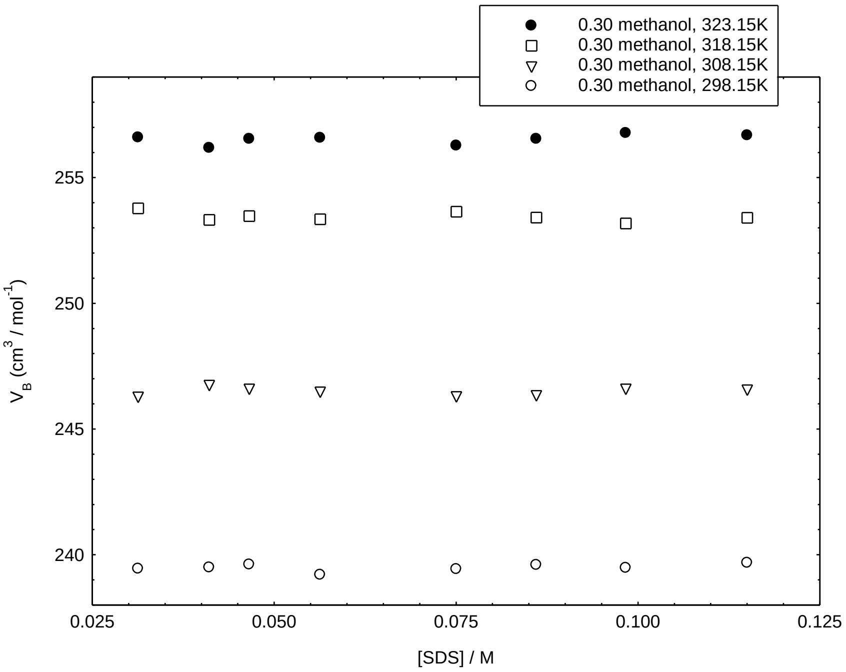


Figure 4.17: Concentration independence of partial molar volume for SDS at different temperature in 0.30 volume fraction of methanol

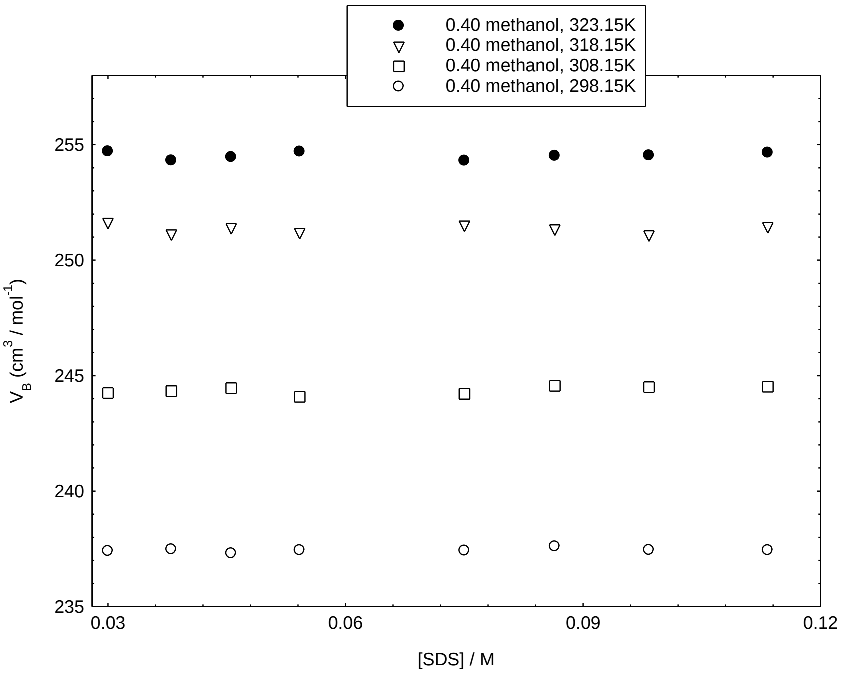


Figure 4.18: Concentration independence of partial molar volume for SDS at different temperature in 0.40 volume fraction of methanol

4.3 Study of Density and Apparent Molar Volume of Sodiumdodecyl Sulphate – Cetyltrimethylammonium Bromide

When methanol and water are mixed they occupy less volume than the sum of their volumes before mixing, in addition, the mixing can resulta temperature change, and also dissolved air may be eliminated.Measurement is made more complex by the fact that mixing ofmethanol and water is exothermic. As a consequence, the mixing effectis reduced in methanol because the expansion due to heating compensates the contraction due to mixing. The mixture was thoroughly shaken and kept 24 hours for the released air bubbles to escape, before attempting to make the solution of cetyltrimethylammonium bromide which was used to make the final solution of sodiumdodecyl sulphate.

The densities for the sodiumdodecyl sulphate in presence of cetyltrimethylammonium bromide in pure water and in four different methanol-water mixtures (containing 0.1, 0.2, 0.3 and 0.4 volume fractions of methanol) at 298.15, 308.15, 318.15, and 323.15 K are depicted in (**Figures 4.19, 4.20, 4.21** and **4.22**).

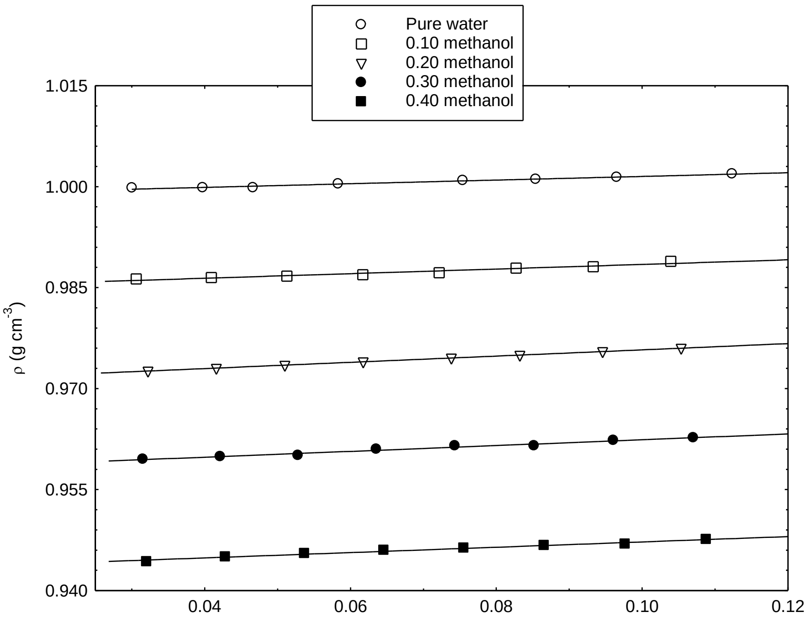


Figure 4.19 Concentration dependence of density for SDS in presence of CTAB at 298.15 K

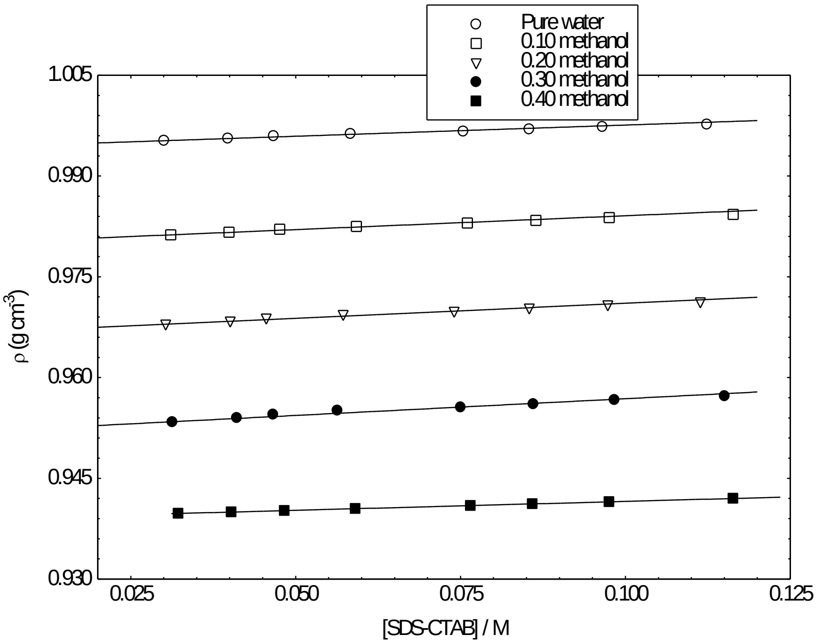


Figure 4.20 Concentration dependence of density for SDS in presence of CTAB at 308.15 K

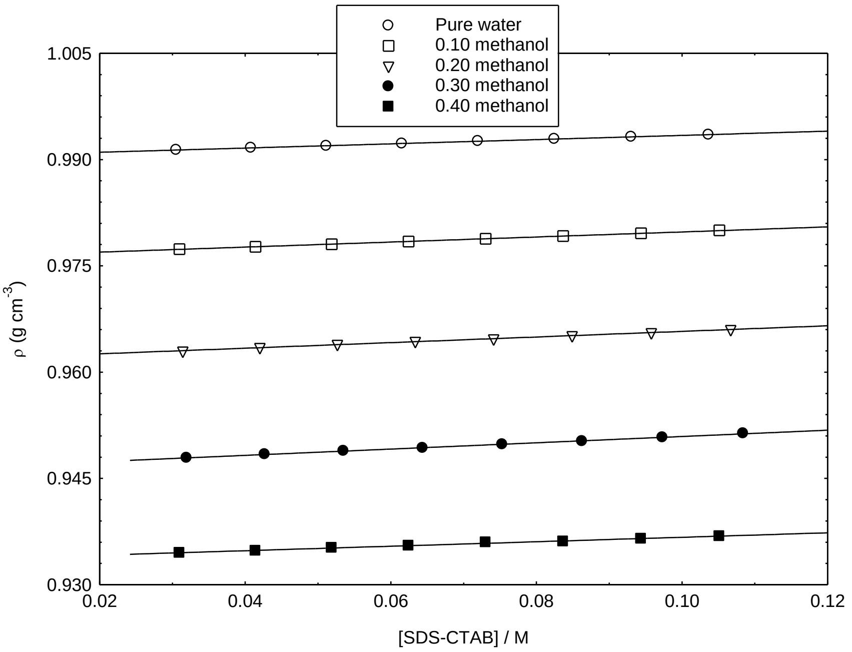


Figure 4.21 Concentration dependence of density for SDS in presence of CTAB at 318.15 K

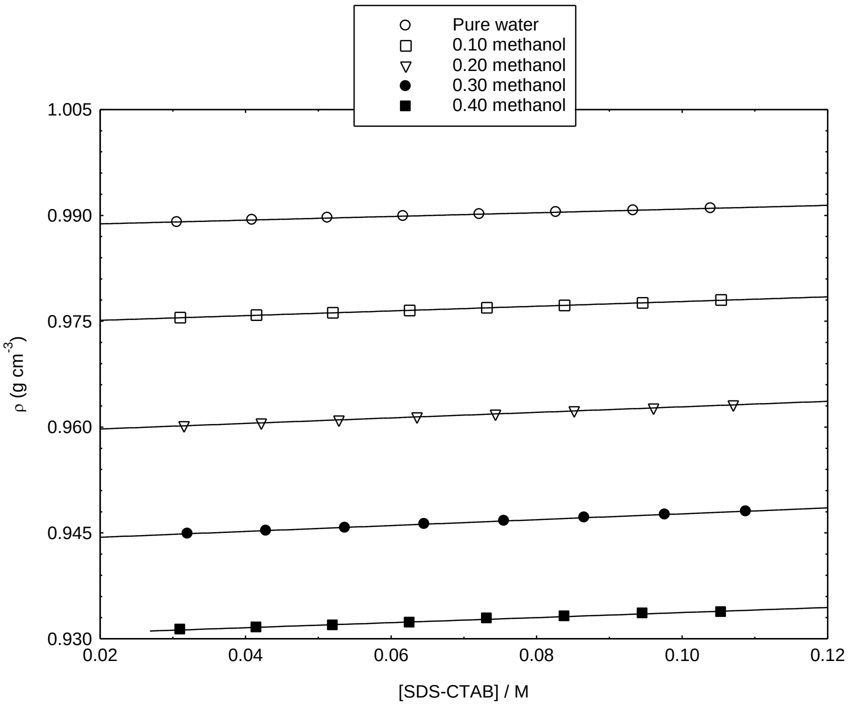


Figure 4.22 Concentration dependence of density for SDS in presence of CTAB at 323.15 K

Figures 4.19, 4.20, 4.21 and **4.22** show the variation of densities of the investigated solutions as a function of the mixed surfactants concentration. From these **figures**, it is evident that the densities exhibit almost increase with increasing concentration within the concentration range investigated here.Our density data of sodiumdodecyl sulphate in presence of cetyltrimethylammonium bromide in pure water and in methanol-water mixtures are found to be higher than the density data of sodiumdodecyl sulphate in pure water and in methanol-water mixtures (Bhattarai *et al.*, 2011; Bhattarai *et al.*, 2013). It is because of the presence of cetyltrimethylammounium bromide with sodiumdodecyl sulphate. It supportsthe mixing of solute naturally increase the density and decrease with increasing temperature (Chauhan *et al.*, 2010).Obviously, the concentration dependence of density follows one and the same pattern at all the temperatures and solvent composition investigated. In fact, the variations of density with mixed surfactants concentrations are always found to be linear.

The slopes of density versus mixed surfactants concentration graph are always found to be positive in methanol-water mixtures, indicating strong ion-ion interactions in these media. The possible explanation for the positive slopes in the present mixed solvent media may be that the counterion binding would become quite appreciable in these media as the concentration of the surfactant is increased,due to weaker ion-solvent interactions. As a consequence, contraction of the solvent would be gradually lowered with increasing concentration of the surfactant, resulting in a net positive volume change per mol of the added surfactant.

The effects of temperature and relative permittivity on the densities values are clearly evident from (**Figures 4.19, 4.20, 4.21** and **4.22**). At each temperature, the density values are found to decrease with decreasing relative permittivity in going from 0.1 volume fraction of methanol to 0.4 volume fractions of methanol over the entire concentration range investigated. The density is found to decrease in a given solvent media, with the increase in temperature as manifested in (**Figures 4.19, 4.20, 4.21** and **4.22**).

The variation of apparent molar volumes for the sodiumdodecyl sulphate in the presence of cetyltrimethylammonium bromidein pure water and four other different methanol+ water mixtures containing (0.10, 0.20, 0.30 and 0.40) volume fraction of methanol at 298.15, 308.15, 318.15, and 323.15 K are as a function of concentration. The representative diagram of such variation is shown in **Figure4.23**.

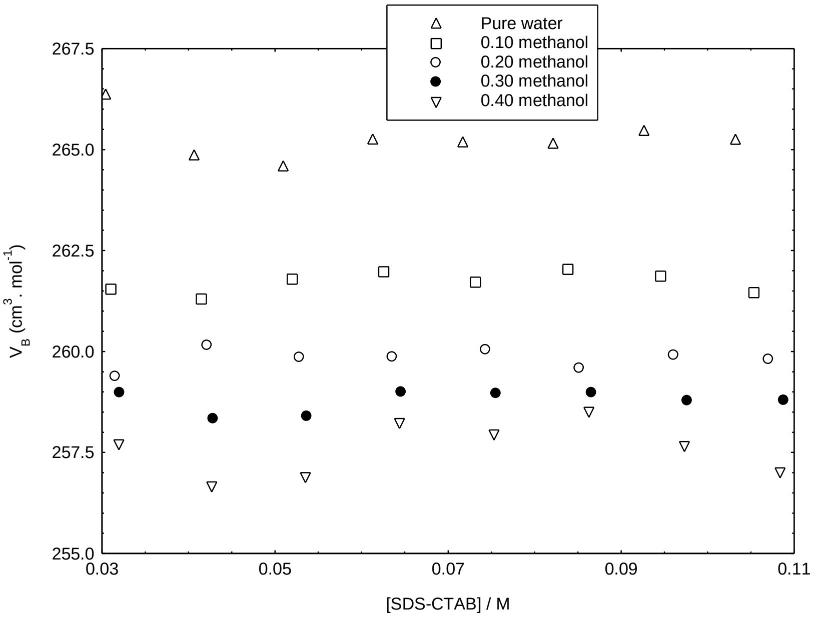


Figure 4.23 Concentration independence of apparent molar volume for SDS in presence of CTAB at 308.15 K

From **Figure 4.23**; the apparent molar volumes exhibit almost the same with increasing concentration within the examined concentration ranges in this study. Actually, in the lower concentration of sodiumdodecyl sulphate in the presence of cetyltrimethylammonium bromide, the apparent molar volumes are concentration dependent. Such behavior was also noticed by De Lisi *et al.*, 1990 while calculating apparent molar volumes of alkyltrimethylammonium bromides. But the apparent molar volumes in the lower concentration of sodiumdodecyl sulphate in the presence of cetyltrimethylammonium bromide was not noted in our investigation because of the irregular pattern of decrease in apparent molar volumes at low concentration of surfactants mixture.

In the examined concentration range, the concentration is almost indepent ofapparent molar volume,the same pattern is followed at all the temperatures and solvent compositions investigated. At each temperature, apparent molar volumes are found to decrease with decreasing relative permittivity by increasing the methanol content in the system. On the other hand, the apparent molar volume is increased in the given system with increasing temperature,this is mostly due to the weakening of surfactant-solvent binding energy with increasing temperature. The same pattern has been reported in the literature (Iqbal and Siddiquah, 2006).

4.4 Study of Conductivity and Related Thermodynamic Properties of Sodiumdodecyl Sulphate in the Absence and Presence of NaCl, NaBr, KCl and KBr

Anionic surfactants are generally carboxylates, sulphates, sulphonates and phosphates. The concentration of surfactant above which a surfactant aggregates into micelles is the cmc (Azum *et al.*, 2017a; Azum et al., 2017b; Azum *et al.*, 2016; Flockhart, 1957; Rosen, 2004; Rub *et al.*, 2016a; Ruckenstein and Nagarajan, 1975). The conductance of ionic surfactants depends on nature of ions formed after dissociation of surfactant, nature of the solvent used, temperature, the presence of additives like salts, etc. The conductivity is determined by plotting specific conductivity against concentration (Rodriguez *et al*., 2003; Williams *et al*., 1955).The formation of micelle is generally occurred at lower concentration (below cmc) than pure surfactant on the addition of an additive like salt (Holmberg *et al*., 2002; Valente *et al*., 2006).The incorporation of additive into an aggregate of an amphiphiles will affect its physicochemical properties such as the degree of dissociation, reaction rates and cloud or phase separation (Azum *et al.*, 2017c; Azum *et al.*, 2016; Azum *et al.*, 2014; Rub *et al.*, 2016b; Schreier *et al.*, 2000).

The plot of specific conductivities with the concentration of sodiumdodecyl sulphate in pure water at 298.15 K is represented in **Figure 4.24**. This plot showed that specific conductance increased with increase in concentration. Such increase in concentrationisexplained due to increase in number of ions per unit volume. **Figure 4.25** represents plots of specific conductance versus concentration of SDS in pure water at 308.15 K in this plot the point of intersection of two lines indicates the critical micelle concentration.

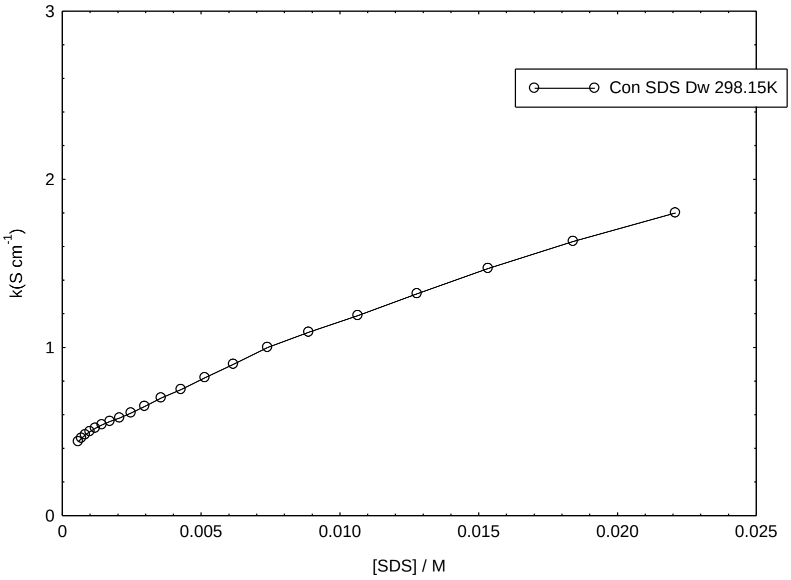


Figure 4.24: Plot of specific conductivity versus concentration of SDS solution at 298.15 K, in pure water

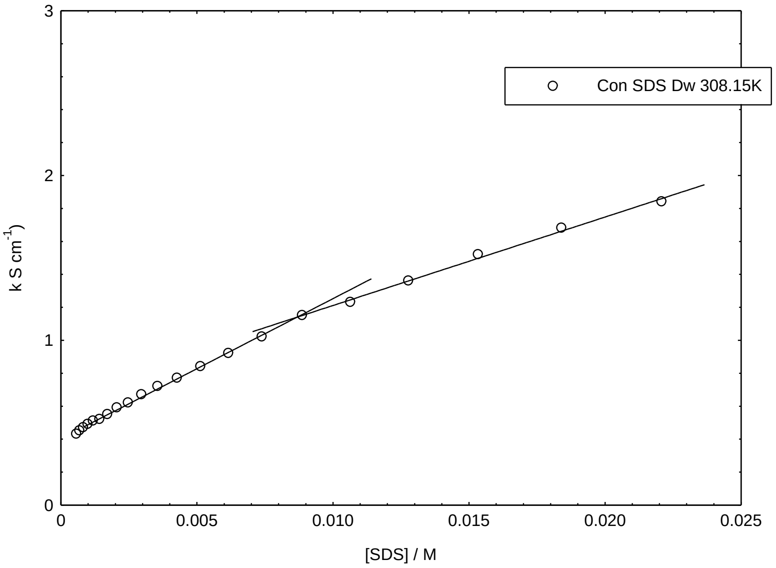


Figure 4.25: Plot of specific conductivity versus concentration of SDS solution at 308.15 K, in pure water, indicating cmc

The plots of specific conductivities with the concentration of sodiumdodecyl sulphate in pure water and in different volume fractions (0.10, 0.20, 0.30 and 0.40) of methanol-water mixtures are depicted in **Figures 4.26**. The point of intersection of two lines of the plot shows cmc. It is observed that the conductivity of surfactant solutions decreased with the increase of volume fraction of methanol in both pre and post micellar region.

We can see the specific conductivity linearly changes with the surfactant concentration in both the pre-micellar and in the post-micellar regions. The slope of pre-micellar (S_2) region is shown to be greater than that in the slope of post-micellar (S_1) region (Bakshi, 1999a).The ratio of S_1 to S_2 gives the value of degree of dissociation of micelle formation,'α' show in equation 4.4.

$$\text{Degree of micelle dissociation, } \alpha = \frac{S_1}{S_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4.4)$$

The decrease ofconductance with the addition of methanol can be explained by two ways; they are structure breaking effect of methanol and increase in viscosity of the medium with the addition of methanol. Such observation was explained by the literature (Naorem and Devi, 2006; Manna and Panda, 2011). The values of the degree of dissociation, 'α' and cmc are presented in table 4.3. The values of cmc and

α for SDS in water are in close resemblance with the data in literature (Dutkiewicz and Jakubowska, 2002).

From the table 4.3, it is found that the cmc, as well as α, increased with the addition of methanol. Such type of results have been reported for the surfactants in alcohol and alcohol-like polar solvent and water mixtures (Akbas and Kartal, 2006; Chung *et al*., 1992; Das *et al*., 2013; Ghosh and Baghel, 2008; Graciani *et al*., 2010; Manna and Panda, 2011; Michor and Berg, 2014; Moya *et al*., 2007; Naorem and Devi, 2006; Nazir *et al*., 2009; Pan *et al*., 2012; Prajapati and Patel, 2012; Ruiz, 1999; Singh and Swarup, 1978; Zana *et al*., 1981).

The micellization of ionic surfactant is responsible for two opposing effects (Wennerstrom and Lindman, 1979). The first effect is the hydrophobic force between the hydrophobic tails attracts the molecules of surfactant or surfactant ions into the micelle core from the aqueous bulk solution. The second effect is related to the ionic head groups, which favor the aqueous bulk phase because the association of surfactant molecules is prevented by the electrostatic repulsive force between the head group.

The degree of dissociation, α, increased with the addition of methanol, which is explained due to the methanol molecules, intercalated between surfactant ions increase the average distance between ionic head groups for steric reasons. This result is decreased in the micellar surface charge density and, in turn, increased dissociation (Zana, 1980).

The other effect deals the relative permittivity of the palisade layer. The palisade layer contains water, ionic head groups, and some counterions in addition to the first two or three methylene groups of the surfactant alkyl chain. On the addition of methanol part of the water in the palisade layer may be replaced by methanol, due to which the relative permittivity of the solvent decreases (Lianos and Zana, 1980).

Withthe increase in temperature, the degree of dissociation 'α' increases. The increase in α can be recognized to the combined effect due to thermal and columbic forces (Kabir-ud-Din *et al*, 2011). Also, temperature effect shows that there is an increase in the degree of dissociation with the increase in the temperature at particular solvent composition. Such behavior indicates that micelles of smaller aggregation number and the higher degree of dissociation are formed at higher temperatures (Mehta *et al.*, 2005).

It is observed that the values of 'α' of SDS are higher in presence of methanol than in absence of it. This may be due to the presence of methanol in the outer portion of the micelle and thus causing steric hindrance to the binding of counterions to the micelle, assisting the dissociation of the counterions, which produces higher α value in the presence of methanol than its absence.

The increase in the degree of dissociation, α, of SDS in the presence of methanol than in pure water is accredited to the solubilization of methanol in the palisade layer of the micelle. The increase of surface area per ionic head group (decrease in the surface charge density), aid the dissociation of the counterion, Na^+, from the micellar head groups of these surfactants, and thereby, giving higher values of 'α' in the presence of methanol. With addition of methanol 'α' value keeps on increasing due to increase in the surface area of the ionic head group (Chauhan *et al.*, 2000; Chung *et al.*, 1992; Dubey, 2008; Kohji and Shigeo, 1977; Kabir-ud-Din *et al.*, 2009; Miyagishi, 1974; Nishikido *et al.*, 1974; Pan *et al.*, 2012; Rodriguez, 2008; Ruiz, 1999; Singh and Swarup, 1979; Sohrabi *et al.*, 2010; Zana, 1980; Zana *et al.*, 1981).

From Table 4.3 as well as **Figure 4.26** shows that the critical micelle concentrations of SDS increase with the increase in volume fraction of methanol. An increase in volume fraction of methanol results increases of cmc at a fixed temperature. Such types of agreement are also found in the literature (Akbas and Kartal, 2006; Chung *et al.*, 1992; Das *et al.*, 2013; Graciani *et al.*, 2010; Ghosh and Baghel, 2008; Manna and Panda, 2011; Michor and Berg, 2014 ; Moya *et al.*, 2007; Naorem and Devi, 2006; Nazir *et al.*, 2009; Pan *et al.*, 2012; Prajapati and Patel, 2012; Ruiz, 1999; Shah *et al.*, 2016; Singh and Swarup, 1978; Zana *et al.*, 1981) for different polar organic solvents in aqueous system.

Electrostatic repulsion between ionic heads and hydrophobic interaction between tails are major factors for micellization (Chandler, 2005; Ghosh, and Baghel 2008). Hydrophobic interaction depends on the relative permittivity of the medium. Water has higher relative permittivity than methanol and when methanol is mixed with water, the relative permittivity of the system decreases (Yilmaz, 2002) due to which hydrophobic interaction becomes less (Moya *et al.*, 2007), that results from the increase in cmc. Because of the lower dielectric constant of the system, the electrostatic repulsion between head group increases. This increase in repulsion can be quantitatively explained by Debye length – the thickness of the ionic atmosphere around each ion in solution (Paria *et al.*, 2004),

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon_r \varepsilon_0 RT}{4\pi F^2 \sum C_i Z_i^2}} \quad \dots\dots\dots\dots\dots\dots (4.5)$$

Here $\frac{1}{\kappa}$is the Debye length, ε_r is the dielectric constant of the solution, ε_0 is the relative permitivity of a vacuum, R is the universal gas constant, T is the absolute temperature, F is the Faraday constant, C_i is the concentration of an ion in solution, and Z_i is charge on the ion. Assuming all the variables constant, a ratio of square roots of relative permitivitycan be used to determine the effect of different solvents on Debye length. In general, a reduction in Debye length will result in an increase in the electrostatic repulsion of head groups (Roebuck *et al.*, 2016) due to which hydrophobic interaction becomes less (Yilmaz, 2002), which eventually increases the cmc (Shah et al., 2016a;Das*et al.*, 2013; Ludzik *et al.*, 2016).

4.4.1 Thermodynamics of Micellization

Following thermodynamic properties are calculated on the basis of pseudo-phase separation model (Shinoda and Hutchinson, 1962; Blandamer *et al.*, 1995; Kim and Lim, 2004) as the standard Gibb's free energy of micellization, $\Delta G_{\mathrm{m}}^{\circ}$, was calculated from the following relation:

$$\Delta G_{\mathrm{m}}^{\mathrm{o}} = (2-\alpha)RT\ \ln X_{\mathrm{cmc}} \quad \dots\dots\dots\dots \quad (4.6)$$

Here X_{cmc} is the mole fraction of surfactant at cmc, R is the universal gas constant and T is the temperature.

The standard enthalpy of micellization ($\Delta H_{\mathrm{m}}^{\circ}$) was calculated from Gibbs-Helmholtz equation as

$$\Delta H_{\mathrm{m}}^{\mathrm{o}} = -RT^2(2-\alpha)\left[{\partial \ln X_{\mathrm{cmc}}}/{\partial T}\right]_{\mathrm{P}} \dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (4.7)$$

The term $\left[\partial \ln X_{\text{cmc}} / \partial T\right]_{\text{P}}$ was calculated by fitting the plot of $\ln X_{\text{cmc}}$ against temperature (**Figure4.27**) and taking the resultant temperature derivative.

The standard entropy of micellization ($\Delta S_{\text{m}}^{\circ}$) was calculated from the following equation as

$$T\Delta S_{\text{m}}^{\text{o}} = \Delta H_{\text{m}}^{\text{o}} - \Delta G_{\text{m}}^{\text{o}} \dots \dots \dots \dots \dots \dots \dots .. (4.8)$$

The standard free energy of transfer ($\Delta G_{\text{trans}}^{\text{o}}$) was calculated from the following equation as

$$\Delta G_{\text{trans}}^{\text{o}} = (\Delta G_{m}^{\text{o}})_{\text{methanol+water}} - (\Delta G_{m}^{\text{o}})_{\text{water}} \dots \dots \dots \dots \dots \dots \dots (4.9)$$

Thermodynamic properties such as standard free energy of micellization ($\Delta G_{\text{m}}^{\circ}$), standard enthalpy of micellization ($\Delta H_{\text{m}}^{\circ}$), the standard entropy of micellization ($\Delta S_{\text{m}}^{\circ}$) and standard free energy of transfer ($\Delta G_{\text{trans}}^{\circ}$) are calculated from equations 4.6 to 4.9 respectively and the values are displayed in Table 4.3 in pure water, 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol at 298.15, 308.15, 318.15 and 323.15 K.

The standard free energy of micellization indicates the spontaneity of micellization process. The spontaneity of micellization will be more when more negative, the standard free energy of micellization change.

From Table 4.3 it is observed that the standard free energy of micellization is negative in water as well as in 0.1, 0.2, 0.3 and 0.4 volume fractions of methanol at 298.15, 308.15, 318.15 and 323.15 K for SDS. It indicates the process of micellization is spontaneous. Again from Table 4.1, $\Delta G_{\text{m}}^{\circ}$ show that negative values of $\Delta G_{\text{m}}^{\circ}$ generally decrease with the addition of methanol in water at 298.15, 308.15, 318.15 and 323.15 K indicating that addition of methanol makes the micellization less favorable.We observed the increase of cmc on increasing the volume fraction of methanol. As a result, the cmc increases is mainly controlled by the variationsin $\Delta G_{\text{trans}}^{\circ}$ (Rodriguez *et al.*, 2008).

It has been concluded that the dependence of the cmc on bulk phase composition is principally controlledby$\Delta G_{\text{trans}}^{\circ}$ changes, produced by the addition of methanol. In a general way, the addition of organic solvent in the bulk phase acts as better solvent for the the surfactantmolecules (Chung *et al*., 1992). This would make the transfer of hydrophobic tail from the bulk phase into the micelle less favorable.As a result$\Delta G^{\circ}_{\mathrm{trans}}$ increases and hence the increase of cmc (Rodriguez*et al*., 2008).Table 4.1 displays that $\Delta G^{\circ}_{\mathrm{trans}}$ increases with the addition of methanol in water signifying the transfer of surfactant tail from bulk into micelle are less favorable.

The values of $\Delta H^{0}_{\mathrm{m}}$ of SDS in aqueous as well as in methanol-water mixture are negative and become more negative with increase in temperature, indicating that the micellization of the SDS is exothermic. The decrease ofΔH^{0}_{m} with the increase of temperature may be due to the destruction of the ordered system due to withdrawing of the hydrogen bond between water molecules surrounding the hydrocarbon chain of the surfactant with increasing temperature (Diamant and Andelman, 2003; Islam and Kato, 2003). The negative values of $\Delta H^{0}_{\mathrm{m}}$ may be taken as proof that London-Dispersion interactions play a more predominant role with the increase of temperature (Ali *et al*., 2014). $\Delta H^{0}_{\mathrm{m}}$ is positively depending upon the structural and solution aspects prevailing in the surfactant solutions in the presence of the additive (Ali *et al*., 2014). Data of this research work are also compared with the micellization behavior of Gemini surfactants in aqueous binary mixtures of dioxane, dimethyl formamide and ethylene glycol (Kabir-ud-Din and Koya, 2010) and found similar behavior on adding the dimethyl formamide form pure water to 0.10 and 0.50 volume fractions of dimethyl formamide in binary mixture of dimethyl formamide-water.

The values of $\Delta S^{0}_{\mathrm{m}}$ are positive for all studied solutions and found to decrease with the addition of methanol. The positive $\Delta S^{0}_{\mathrm{m}}$ indicates micellization process is favored with the increase of entropy (Kabir-ud-Din and Koya, 2010). Similar behaviour was observed in literature (Akbas and Kartal, 2006; Chaudhary and Pal, 2014; Ruiz, 1999). It is found that the $\Delta S^{0}_{\mathrm{m}}$decreased with increase of temperature indicating the disordering of water molecules becomes less pronounced due to the destruction of the iceberg water structure around the alkyl group with increasing temperature. Such behaviors were also observed in literatures (Akbas and Kartal, 2006; Ruiz, 1999; Kabir-ud-Din and Koya, 2010).

In all cases, the ΔG^0_{trans} values are positive and found similar behavior in the literature (Michele *et al.*, 2011; Ruiz, 1999). The $\Delta G^0_{\mathrm{trans}}$ value regularly increases with the addition of methanol at investigated temperature.

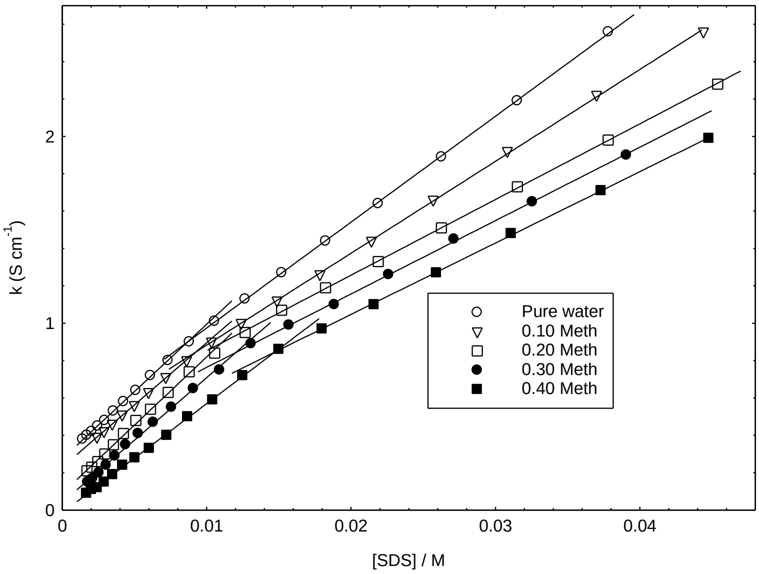


Figure 4.26: Specific conductance of SDS versus concentration in pure water at 308.15 K: The breaking points indicating the critical micelle concentration

Figure 4.26 displays the representing graphs for SDS solutions in absence of salts in water, 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol-water are measured at 308.15 K. It is seen from the **figure 4.26** that conductivity decreases with increase in volume fraction of methanol. It is due to decrease in relative permittivity and increase in viscosity of the medium which eventually resulted in the decrease in conductivity (Manna and Panda, 2011).

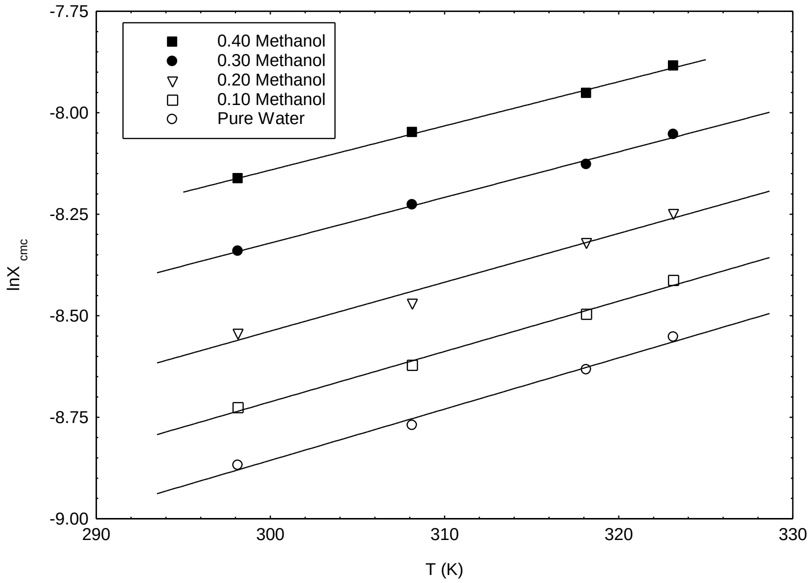


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Figure 4.27: Plot of variation of $\ln X_{cmc}$ with temperature for SDS

In **Figure 4.27**, the variation of $\ln X_{cmc}$ with temperature for SDS shows the linear plots. The term

$\left[\partial \ln X_{\mathrm{cmc}} / \partial T\right]_{\mathrm{P}}$ was obtained by fitting the plot of $\ln X_{cmc}$ versus temperature for SDS and taking the corresponding temperature derivative.

Table 4.3 Critical micelle concentration, degree of micelle dissociation, standard free energy of micellization, standard enthalpy of micellization, standard entropy of micellization and standard free energy transfer of SDS in water, 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol-water mixture measured at 298.15, 308.15, 318.15 and 323.15 K*

T/K	Vol. fraction of methanol	cmc/mM	α	$\Delta G^{\circ}_{\mathrm{m}}$ $(\mathrm{kJmol^{-1}})$	$\Delta H^{\circ}_{\mathrm{m}}$ $(\mathrm{kJmol^{-1}})$	$\Delta S^{\circ}_{\mathrm{m}}$ $(\mathrm{Jmol^{-1}K^{-1}})$	$\Delta G^{\circ}_{\mathrm{trans}}$ $(\mathrm{kJmol^{-1}})$
298.15	0.0	7.8	0.45	-34.07	-14.49	65.67	--
	0.1	8.5	0.46	-33.31	-14.15	64.28	0.76
	0.2	9.6	0.47	-32.40	-13.63	62.94	1.67
	0.3	11.0	0.48	-31.43	-12.68	62.89	2.64
	0.4	12.3	0.50	-30.35	-12.09	61.25	3.72
308.15	0.0	8.6	0.52	-33.25	-14.77	59.97	--
	0.1	9.4	0.54	-32.25	-14.32	58.17	1.00
	0.2	10.3	0.56	-31.24	-13.69	56.94	2.01
	0.3	12.3	0.58	-29.93	-12.62	56.16	3.32
	0.4	13.7	0.6	-28.87	-12.04	54.62	4.38
318.15	0.0	9.8	0.55	-33.11	-15.37	55.75	--
	0.1	10.6	0.57	-32.14	-14.89	54.19	0.97
	0.2	11.9	0.59	-31.03	-14.27	52.65	2.08
	0.3	13.5	0.61	-29.88	-13.13	52.66	3.23
	0.4	15.0	0.63	-28.82	-12.56	51.08	4.29
323.15	0.0	10.6	0.56	-33.09	-15.80	53.48	--
	0.1	11.5	0.58	-32.09	-15.31	51.93	0.99
	0.2	12.8	0.60	-31.02	-14.64	50.68	2.06
	0.3	14.5	0.62	-29.86	-13.48	50.66	3.23
	0.4	16.0	0.64	-28.81	-12.86	49.36	4.28

*The error limits of α, CMC,$\Delta G^{o}_{\mathrm{m}}$, $\Delta H^{o}_{\mathrm{m}}$,$\Delta S^{o}_{\mathrm{m}}$ and $\Delta G^{o}_{\mathrm{trans}}$ are ±5, ±5, ±3, ±4, ±3, and ±5% respectively.

Table 4.4 Critical micelle concentration, degree of micelle dissociation, standard free energy of micellization, standard enthalpy of micellization, standard entropy of micellization and standard free energy transfer of SDS with NaCl in water, 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol-water mixture measured at 298.15, 308.15, 318.15 and 323.15 K*****

T / K	Vol. fraction of methanol	cmc /mM	α	$\Delta G^{\circ}_{\mathrm{m}}$ $(\mathrm{kJmol^{-1}})$	$\Delta H^{\circ}_{\mathrm{m}}$ $(\mathrm{kJmol^{-1}})$	$\Delta S^{\circ}_{\mathrm{m}}$ $(\mathrm{Jmol^{-1}K^{-1}})$	$\Delta G^{\circ}_{\mathrm{trans}}$ $(\mathrm{kJmol^{-1}})$
298.15	0.0	5.3	0.53	-33.72	-18.86	49.83	--
	0.1	6.5	0.54	-32.55	-17.73	49.70	1.17
	0.2	7.3	0.55	-31.69	-17.16	48.71	2.03
	0.3	8.5	0.56	-30.69	-16.80	46.59	3.02
	0.4	9.6	0.57	-29.80	-16.25	45.46	3.91
308.15	0.0	6.4	0.55	-33.68	-19.80	45.03	--
	0.1	7.7	0.56	-32.53	-18.66	44.99	1.15
	0.2	8.6	0.57	-31.68	-18.06	44.18	2.00
	0.3	10.0	0.58	-30.68	-17.68	42.17	3.00
	0.4	11.3	0.59	-29.78	-17.30	40.50	3.89
318.15	0.0	7.5	0.57	-33.66	-20.74	40.61	--
	0.1	9.0	0.58	-32.53	-19.61	40.58	1.14
	0.2	10.0	0.59	-31.67	-18.95	39.96	1.99
	0.3	11.6	0.60	-30.66	-18.55	38.05	3.00
	0.4	13.0	0.61	-29.76	-18.12	36.57	3.90
323.15	0.0	8.1	0.58	-33.65	-21.22	38.46	--
	0.1	9.7	0.59	-32.51	-20.08	38.45	1.14
	0.2	10.8	0.6	-31.65	-19.39	37.93	1.99
	0.3	12.5	0.61	-30.64	-18.96	36.13	3.01
	0.4	14.0	0.62	-29.74	-18.49	34.79	3.91

*The error limits of α, CMC,$\Delta G^{\mathrm{o}}_{\mathrm{m}}$, $\Delta H^{\mathrm{o}}_{\mathrm{m}}$,$\Delta S^{\mathrm{o}}_{\mathrm{m}}$ and $\Delta G^{\mathrm{o}}_{\mathrm{trans}}$ are ±4, ±5, ±4, ±3, ±5, and ±5% respectively.

Table 4.5 Critical micelle concentration, degree of micelle dissociation, standard free energy of micellization, standard enthalpy of micellization, standard entropy of micellization and standard free energy transfer of SDS with NaBr in water, 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol-water mixture measured at 298.15, 308.15, 318.15 and 323.15 K*

T/K	Vol. fraction of methanol	cmc/mM	α	$\Delta G^{\circ}_{\mathrm{m}}$ $(\mathrm{kJmol^{-1}})$	$\Delta H^{\circ}_{\mathrm{m}}$ $(\mathrm{kJmol^{-1}})$	$\Delta S^{\circ}_{\mathrm{m}}$ $(\mathrm{Jmol^{-1}K^{-1}})$	$\Delta G^{\circ}_{\mathrm{trans}}$ $(\mathrm{kJmol^{-1}})$
298.15	0.0	5.0	0.6	-32.32	-17.96	48.13	--
	0.1	6.2	0.61	-31.15	-16.87	47.87	1.16
	0.2	6.8	0.62	-30.40	-16.33	47.18	1.91
	0.3	7.7	0.63	-29.54	-15.98	45.45	2.77
	0.4	9.0	0.64	-28.56	-15.46	43.96	3.75
308.15	0.0	6.2	0.62	-32.15	-18.73	43.54	--
	0.1	7.3	0.63	-31.14	-17.75	43.44	1.00
	0.2	8.1	0.64	-30.36	-17.17	42.79	1.79
	0.3	9.0	0.65	-29.52	-16.81	41.25	2.63
	0.4	10.5	0.66	-28.55	-16.44	39.31	3.59
318.15	0.0	7.3	0.64	-32.14	-19.60	39.40	--
	0.1	8.5	0.65	-31.12	-18.61	39.34	1.01
	0.2	9.4	0.66	-30.34	-18.01	38.75	1.79
	0.3	10.4	0.67	-29.51	-17.62	37.36	2.62
	0.4	12.0	0.68	-28.54	-17.21	35.61	3.59
323.15	0.0	7.8	0.65	-32.13	-20.05	37.38	--
	0.1	9.2	0.66	-31.09	-19.04	37.28	1.04
	0.2	10.0	0.67	-30.34	-18.52	36.56	1.79
	0.3	11.2	0.68	-29.49	-18.12	35.17	2.64
	0.4	13.0	0.69	-28.47	-17.55	33.79	3.65

*The error limits of α, CMC,$\Delta G^{\mathrm{o}}_{\mathrm{m}}$, $\Delta H^{\mathrm{o}}_{\mathrm{m}}$,$\Delta S^{\mathrm{o}}_{\mathrm{m}}$ and $\Delta G^{\mathrm{o}}_{\mathrm{trans}}$ are ±3, ±4, ±5, ±4, ±3, and ±5% respectively.

Table 4.6 Critical micelle concentration, degree of micelle dissociation, standard free energy of micellization, standard enthalpy of micellization, standard entropy of micellization and standard free energy transfer of SDS with KCl in water, 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol-water mixture measured at 298.15, 308.15, 318.15 and 323.15 K*

T/K	Vol. fraction of methanol	cmc/mM	α	$\Delta G^{\circ}_{\mathrm{m}}$ $(\mathrm{kJmol^{-1}})$	$\Delta H^{\circ}_{\mathrm{m}}$ $(\mathrm{kJmol^{-1}})$	$\Delta S^{\circ}_{\mathrm{m}}$ $(\mathrm{Jmol^{-1}K^{-1}})$	$\Delta G^{\circ}_{\mathrm{trans}}$ $(\mathrm{kJmol^{-1}})$
298.15	0.0	2.9	0.32	-41.08	-21.56	65.47	--
	0.1	4.0	0.33	-39.26	-20.27	63.67	1.82
	0.2	4.9	0.34	-37.88	-19.65	61.16	3.19
	0.3	6.0	0.35	-36.59	-19.25	58.14	4.48
	0.4	7.2	0.36	-35.33	-18.64	55.97	5.74
308.15	0.0	3.9	0.34	-40.64	-22.73	58.11	--
	0.1	5.1	0.35	-39.05	-21.32	57.54	1.58
	0.2	6.0	0.36	-37.86	-20.71	55.65	2.77
	0.3	7.2	0.37	-36.59	-20.29	52.86	4.05
	0.4	8.7	0.38	-35.29	-19.88	49.99	5.35
318.15	0.0	4.9	0.36	-40.45	-23.87	52.11	--
	0.1	6.1	0.37	-39.01	-22.47	51.99	1.44
	0.2	7.3	0.38	-37.74	-21.77	50.18	2.71
	0.3	8.6	0.39	-36.55	-21.33	47.84	3.89
	0.4	10.3	0.4	-35.24	-20.86	45.19	5.21
323.15	0.0	5.4	0.37	-40.40	-24.49	49.24	--
	0.1	6.7	0.38	-38.99	-23.08	49.27	1.40
	0.2	8.0	0.39	-37.69	-22.42	47.24	2.71
	0.3	9.4	0.4	-36.48	-21.97	44.89	3.92
	0.4	11.2	0.41	-35.22	-21.31	43.05	5.18

*The error limits of α, CMC,$\Delta G^{\mathrm{o}}_{\mathrm{m}}$, $\Delta H^{\mathrm{o}}_{\mathrm{m}}$,$\Delta S^{\mathrm{o}}_{\mathrm{m}}$ and $\Delta G^{\mathrm{o}}_{\mathrm{trans}}$ are ±5, ±3, ±4, ±5, ±3, and ±5% respectively.

Table 4.7 Critical micelle concentration, degree of micelle dissociation, standard free energy of micellization, standard enthalpy of micellization, standard entropy of micellization and standard free energy transfer of SDS with KBr in water, 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol-water mixture measured at 298.15, 308.15, 318.15 and 323.15 K*

T/K	Vol. fraction of methanol	cmc/mM	α	$\Delta G^{\circ}_{\mathrm{m}}$ $(\mathrm{kJmol^{-1}})$	$\Delta H^{\circ}_{\mathrm{m}}$ $(\mathrm{kJmol^{-1}})$	$\Delta S^{\circ}_{\mathrm{m}}$ $(\mathrm{Jmol^{-1}K^{-1}})$	$\Delta G^{\circ}_{\mathrm{trans}}$ $(\mathrm{kJmol^{-1}})$
298.15	0.0	2.3	0.56	-36.07	-18.48	59.02	--
	0.1	2.9	0.57	-34.74	-17.36	58.28	1.33
	0.2	3.7	0.58	-33.47	-16.81	55.89	2.60
	0.3	4.3	0.59	-32.43	-16.45	53.61	3.63
	0.4	4.7	0.6	-31.68	-15.91	52.88	4.39
308.15	0.0	2.9	0.58	-35.82	-19.44	53.15	--
	0.1	3.8	0.59	-34.37	-18.21	52.43	1.45
	0.2	4.4	0.6	-33.44	-17.68	51.13	2.38
	0.3	5.1	0.61	-32.40	-17.31	48.99	3.41
	0.4	5.5	0.62	-31.67	-16.93	47.83	4.15
318.15	0.0	3.8	0.6	-35.47	-20.26	47.81	--
	0.1	4.6	0.61	-34.34	-19.14	47.79	1.12
	0.2	5.4	0.62	-33.27	-18.55	46.29	2.19
	0.3	6.0	0.63	-32.39	-18.15	44.74	3.08
	0.4	6.4	0.64	-31.66	-17.73	43.79	3.80
323.15	0.0	4.2	0.61	-35.39	-20.69	45.48	--
	0.1	5.0	0.62	-34.31	-19.62	45.46	1.08
	0.2	5.8	0.63	-33.23	-19.08	43.80	2.15
	0.3	6.6	0.64	-32.30	-18.67	42.16	3.09
	0.4	6.9	0.65	-31.64	-18.09	41.93	3.74

*The error limits of α, CMC,$\Delta G^{\mathrm{o}}_{\mathrm{m}}$, $\Delta H^{\mathrm{o}}_{\mathrm{m}}$,$\Delta S^{\mathrm{o}}_{\mathrm{m}}$ and $\Delta G^{\mathrm{o}}_{\mathrm{trans}}$ are ±4, ±5, ±3, ±4, ±5, and ±5% respectively.

The decrease in values of cmc of SDS in the presence of monovalent salts (NaCl, NaBr, KCl and KBr) at tables 4.2, 4.3, 4.4 and 4.5 can also show the similar patterns with the increase in values of cmc of SDS with the increase in methanol content. From Tables 4.1-4.5, the variation of the cmc of SDS in the presence and absence of monovalent salts as in the order: Water > NaCl > NaBr > KCl > KBr. Such variation in the cmc of SDS in NaCl and KCl was also found in the literature (Dutkiewicz and Jakubowska, 2002). The reason of decreasing cmc of SDS in the presence of salts is due to the salt ions added to the solution interact with head groups of the surfactant (Kontogeorgis and Kiil, 2016). The cmc of SDS in the presence of NaCl, NaBr, KCl and KBr are in the order cmc $_{(NaCl)}$ > cmc $_{(NaBr)}$ > cmc $_{(KCl)}$ > cmc $_{(KBr)}$. Regarding the standard free energy of micellization of SDS in the presence of monovalent salts, the standard free energy of micellization becomes more negative in KCl and KBr whereas the less negative in NaCl and NaBr. It is seen from the data in tables 4.1 to 4.5 that the standard free energy of micellization is negative in water as well as in methanol-water mixed solvent media at investigated temperatures.

A negative value of $\Delta G^{\circ}_{\mathrm{m}}$ decreases with the increase in volume fractions of methanol at particular temperature indicating that addition of methanol makes the micellization less favorable also in the case of monovalent salts. It is believed that the micelles are formed from ionic surfactants is due to the fact that hydrophobic driving force competes with the electrostatic repulsion arising from ionic heads (Kronberg *et al.*, 1995). On the same point, when methanol is added in water, the relative permittivity of the medium decreases and the medium becomes more hydrophobic due to which the driving force for micellization decreases. It is seen that with the increase in temperature $\Delta G^{\circ}_{\mathrm{m}}$ values become less negative indicating less spontaneity of micellization at the higher temperature. This phenomenon can be attributed to the agitation of the micelle due to thermal forces at the higher temperature (Ali *et al.*, 2014).

According to the theory of surfactant self-assembly (Nagarajan and Wang, 2000), the major contribution to the standard free energy of micellization is associated with the transfer of the surfactant tail from solvent into the micelle$\Delta G^{\circ}_{\mathrm{trans}}$. The $\Delta G^{\circ}_{\mathrm{trans}}$ values in Tables 4.1 to 4.5 are all positive and increase with the increasing volume fraction of methanol in water indicating the transfer of the surfactant tail from the bulk into the micelle is less favorable in all the cases of salts present in SDS solutions.

The values of$\Delta H^{\circ}_{\mathrm{m}}$ of SDS in aqueous as well as in methanol-water in the presence of salts are negative and become more negative with the rise in temperature, suggesting that the micellization of the surfactant is exothermic. The observed decrease of $\Delta H^{\circ}_{\mathrm{m}}$

with temperature is probably due to the destruction of the ordered aqueous region due to the diminishing of the hydrogen bond between water molecules surrounding the hydrocarbon chain of the surfactant with increasing temperature (Islam and Kato, 2003).

$\Delta S^{\circ}_{\mathrm{m}}$ Values decreased with the increase in volume fraction of methanol in all the cases of salts presence. The positive entropy change indicates micellization process is favored by entropy gain, associated with the destruction of the iceberg around the hydrophobic alkyl chain, pre-requisite condition for the micelle formation. As the temperature is increased the $\Delta S^{\circ}_{\mathrm{m}}$ showed a decreasing trend. This implies that disordering of water molecules becomes less pronounced due to the destruction of the iceberg water structure around the alkyl group with increasing temperature (Kabir-ud-Din and Koya, 2010).

The variation of both $\Delta H^{\circ}_{\mathrm{m}}$ and $\Delta S^{\circ}_{\mathrm{m}}$ values showed a mutual relationship of enthalpy-entropy compensation phenomenon. When the enthalpy contributes less $\Delta G^{\circ}_{\mathrm{m}}$, its counter-part noted as $\Delta S^{\circ}_{\mathrm{m}}$contributes more in order to lead-free energy to show large negative value and vice versa. The **Figure 4.28** shows such relationship for SDS in NaCl system with water and methanol-water mixed solvent media at 298.15 K.

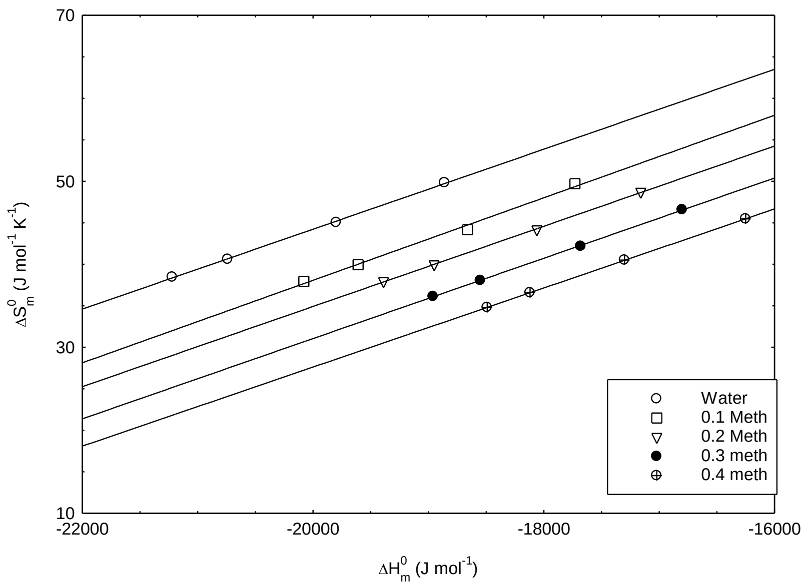

Figure 4.28: $\Delta S^{\circ}_{\mathrm{m}}$versus $\Delta H^{\circ}_{\mathrm{m}}$ for SDS with NaCl system in pure water and four different volume fractions of methanol at 298.15 K

A linear relationship was obtained for $\Delta H^{\circ}_{\mathrm{m}} - \Delta S^{\circ}_{\mathrm{m}}$ and is expressed with the help of equation (4.10).

$$\Delta S_{\mathrm{m}}^{\circ} = \frac{1}{T_{\mathrm{c}}} \Delta H_{\mathrm{m}}^{\circ} + \sigma \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (4.10)$$

Where $1/T\mathrm{c}$ is the slope of the compensation plot and σ is intercept of the linear plot. T_{c} is the compensation temperature, can be interpreted as a characteristic of solute-solute and solute-solvent interactions, i.e., proposed as a measure of the "desolvation" part of the process of micellization. The intercept σ characterizes the solute-solute interaction, i.e., considered as an index of the "chemical" part of the process of micellization (Chen *et al.*, 1998). The values of $T\mathrm{c}$, σ and $\Delta_{\mathrm{m}}C_{\mathrm{p}}^{\circ}$for SDS in absence and presence of salts using conductivity measurement are given in Table 4.8.

Table 4.8 Values of T_{c}, σ and $\Delta_{\mathrm{m}}C_{\mathrm{p}}^{\circ}$ for SDS in water and methanol-water of NaCl, NaBr, KCl and KBr using conductivity measurement

Compensation parameters	SDS	SDS in NaCl	SDS in NaBr	SDS in KCl	SDS in KBr
T_{c} (K) [Pure water]	114.68	207.47	194.93		
σ(kJ mol^{-1}K^{-1})	190	141	140	180.83	162.07
$\Delta_{\mathrm{m}}C_{\mathrm{p}}^{\circ}$ (J.mol^{-1}K^{-1})	-52.10	-94.30	-83.60	184	173
				-117.00	-88.00
T_{c} (K)[0.1 Methanol]	105.82	210.08	204.92	195.31	177.94
σ(kJ mol^{-1}K^{-1})	196	134	130	167	155
$\Delta_{\mathrm{m}}C_{\mathrm{p}}^{\circ}$ (J.mol^{-1}K^{-1})	-46.40	-94.50	-86.60	-112.00	-90.50
T_{c}(K)[0.2 Methanol]	98.04	207.47	205.34	198.41	186.57
σ(kJ mol^{-1}K^{-1})	199	131	127	160	146
$\Delta_{\mathrm{m}}C_{\mathrm{p}}^{\circ}$ (J.mol^{-1}K^{-1})	-41.10	-89.40	-86.60	-110.00	-89.90
T_{c}(K)[0.3 Methanol]	93.46	206.61	207.47	204.92	194.17
σ(kJ mol^{-1}K^{-1})	195	128	122	152	138
$\Delta_{\mathrm{m}}C_{\mathrm{p}}^{\circ}$ (J.mol^{-1}K^{-1})	-32.80	-86.60	-84.60	-107.00	-87.90
T_{c}(K) [0.4 Mthanol]	91.74	210.08	207.47	206.19	199.20
σ(kJ mol^{-1}K^{-1})	190	123	119	146	133
$\Delta_{\mathrm{m}}C_{\mathrm{p}}^{\circ}$ (J.mol^{-1}K^{-1})	-32.10	-89.40	-83.70	-106.00	-87.00

The error limits of T_{c}, σ and $\Delta_{\mathrm{m}}C_{\mathrm{p}}^{\circ}$ are ±4, ±5, and ±5% respectively.

Temperature dependence of hydrophobic effect expressed as heat capacity of micellization$(\Delta_\mathrm{m}C_\mathrm{p}^\circ)$and estimated from slope of $\Delta H_\mathrm{m}^\circ$ vs temperature curve for SDS in presence of NaCl (**Figure 4.29**) is noted as under

$$\Delta_\mathrm{m}C_\mathrm{p}^\circ = \frac{\partial \Delta_\mathrm{m}H^\circ}{\partial T} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.11)$$

The $\Delta_\mathrm{m}C_\mathrm{p}^\circ$ values are negative, as usually observed for the self-association of amphiphiles and ascribed to the removal of large areas of nonpolar surface from contact with water on micelle formation.

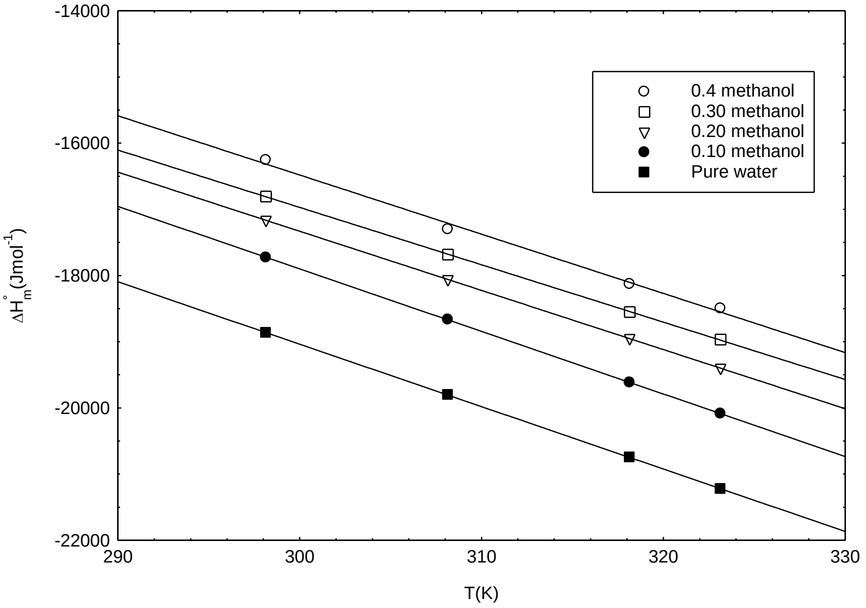

Figure 4.29: ΔH_m° versus T K for SDS with NaCl in pure water and four different volume fractions of methanol at 298.15 K

The variation of T_c in the absence and presence of salts in water and methanol-water mixture is in the following order. T_c has been increased from the absence of salt**s** to the presence of NaCl and then almost decreased in NaBr, KCl and KBr system. Such variations of T_c are also found in 0.1, 0.2, 0.3 and 0.4 volume fractions of methanol. Moreover, T_c has been observed higher in SDS + water whereas lower in the mixture (SDS + methanol-water) in descending order of 0.1, 0.2, 0.3 and 0.4 volume fractions of methanol both in presence and absence of salts as shown in **Figure 4.30**.

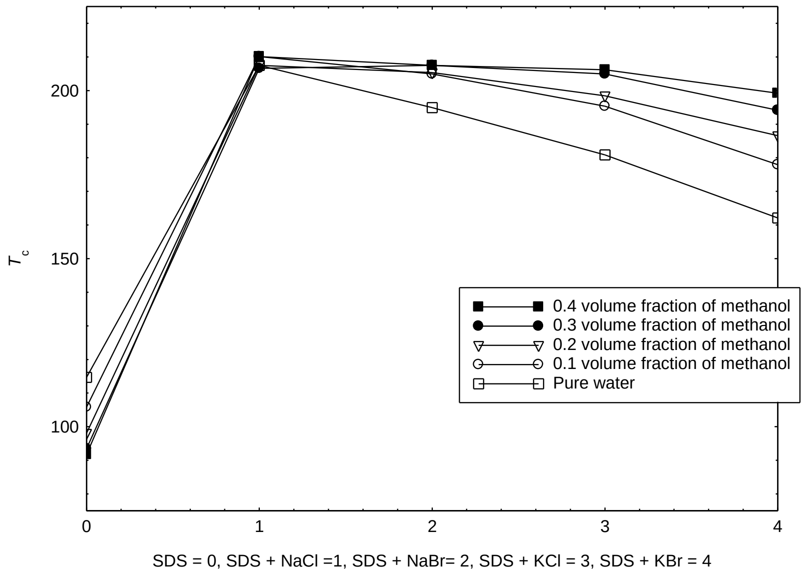

Figure 4.30: T_c versus SDS in the absence and presence of NaCl, NaBr, KCl and KBr system in water and 0.1, 0.2, 0.3 and 0.4 volume fraction of methanol in methanol-water mixed solvent media

From Table 4.8 only SDS system, when methanol increases from water, the presence of the co-solvent produces a less structured medium, where the solvophobic interactions are considerably reduced (Ruiz *et al.*, 2008). Again from the same Table 4.8 of SDS in NaCl system, it is to be noted that the *T*c values that we have found in water and 0.1, 0.2, 0.3 and 0.4 volume fractions of methanol falls into the suggested range of 207-211 K. This fact can be interpreted in the sense that the micellizaton process of SDS in the 0.1, 0.2, 0.3 and 0.4 volume fractions of methanol occurs under the same structural conditions that in pure water and for SDS in NaBr, KCl and KBr follow the same trends of SDS in NaCl after 0.1 volume fraction of methanol whereas for water to 0.1 volume fraction of methanol for SDS in NaBr, KCl and KBr systems, the presence of the co-solvent produces a less structured medium, where the solvophobic interactions are considerably reduced.

The variation of σ in the absence and presence of salts in water and methanol-water mixture is in the following order.Value of σ decreases in presence of salt than in absence of salt. σ has been decreased from the absence of salts to the presence of NaCl and NaBr and then increased in the presence of KCl and further almost decreased in KBr system. Such variations of σ are also found in 0.1, 0.2, 0.3 and 0.4 volume fractions of methanol. Moreover, σ has been observed lower in (SDS + water) whereas higher in (SDS + methanol-water mixture). But σ has been observed higher in SDS + salts in water whereas lower in SDS + methanol-water mixture in the ascending order in addition of methanol as 0.1, 0.2, 0.3 and 0.4 volume fractions of methanol as shown in **Figure 4.31.**

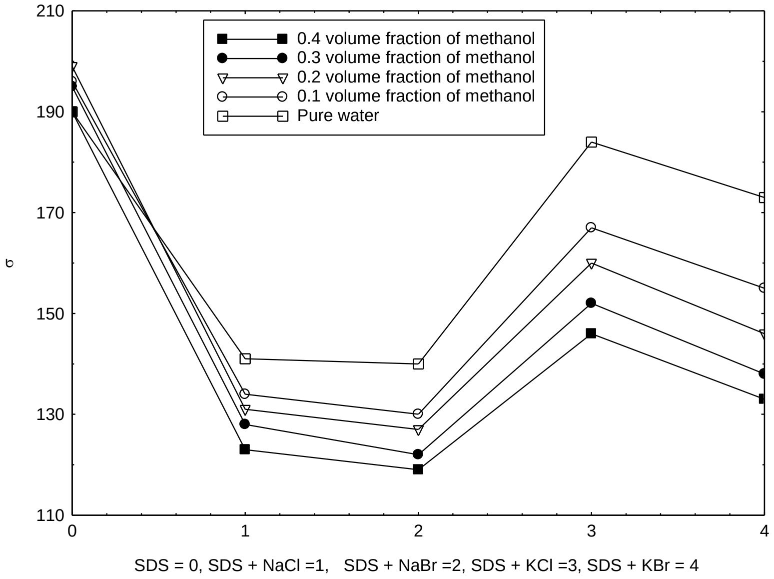

Figure 4.31: σ versus SDS in the absence and presence of NaCl, NaBr, KCl and KBr system in water and 0.1, 0.2, 0.3 and 0.4 volume fraction of methanol in methanol-water mixed solvent media

4.4.2 Correlation of $\Delta G_{\mathrm{m}}^{\circ}$with Solvent Parameters

Our focus is to correlate $\Delta G_{\mathrm{m}}^{\circ}$with different solvent parameters namely the relative permittivity, the Reichardt's parameter (Fuoss and Kraus, 1933), the Hildebrandparameter (Hildebrand and Scott, 1964; Paruta *et al.*, 1962; Lordi *et al.*, 1964), and the Gordon parameter (Sjober *et al.*, 1990).

It can be observed that micellization consists of molecular association, the fluidity, polarity and solvent structure (Pan *et al.*, 2012). We use the methanol-water mixture to see the effect of SDS in the presence and absence of salts on the $\Delta G_{\mathrm{m}}^{\circ}$ values. *D*, *G* and δ of methanol-water mixtures are presented. The δ, *D*and *G* values were taken from the literature (Shah *et al.*, 2016) and δ values were evaluated with the popular relationship given elsewhere (Paruta *et al.* 1962; Lordi *et al.*, 1964; Marcus, 1985) between δ and relative permittivity.

$$\delta = 0.45D + 18.5 \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (4.12)$$

All parameters produced curvilinear correlations with$\Delta G^{\circ}_{\mathrm{m}}$. For SDS curves in the presence and absence of salts were concave in the methanol-water mixture. Such types of trends were also observed by Pan *et al.*, 2012 for $\Delta G^{\circ}_{\mathrm{m}}$ with solvent parameters in SDS in methanol-water and dioxane-water at 303.15 K. Das and Das, 2009 found linear relations between $\Delta G^{\circ}_{\mathrm{m}}$ and *G* but the points in the plots were widely scattered.

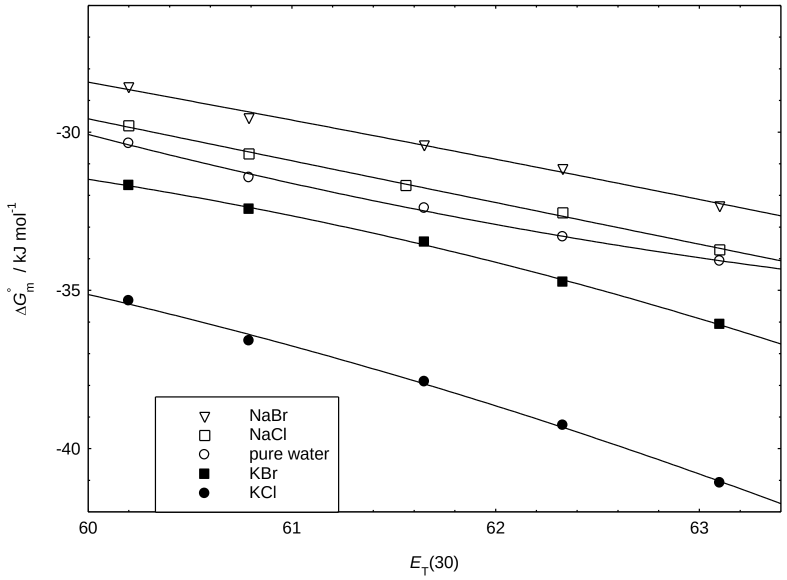

Figure. 4.32: $\Delta G^{\circ}_{\mathrm{m}}$ versus E_{T} (30) for SDS in absence and presence of salts

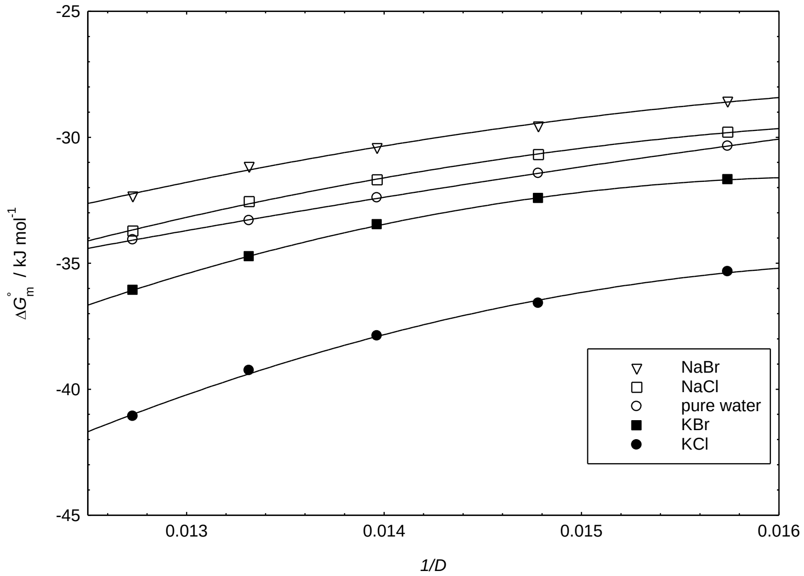

Figure. 4.33: $\Delta G^{\circ}_{\mathrm{m}}$ versus 1/D for SDS in absence and presence of salts

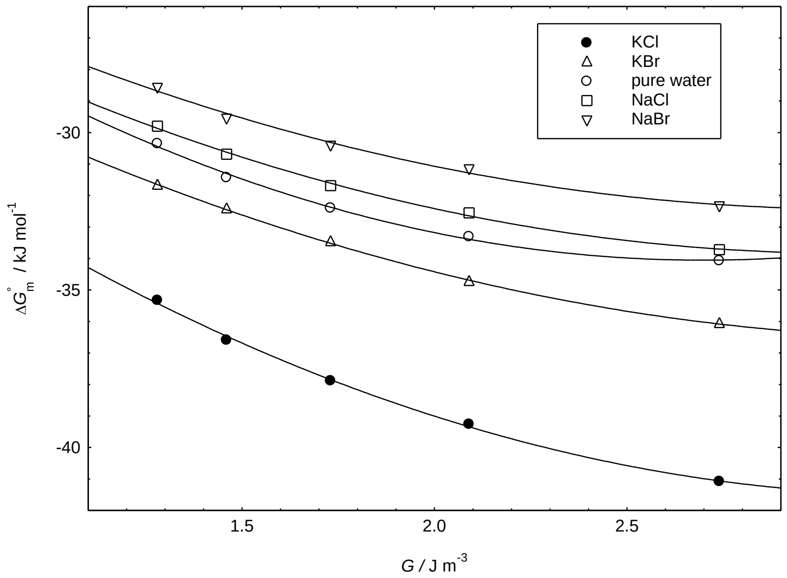

Figure. 4.34: $\Delta G^\circ_\mathrm{m}$ versus G for SDS in absence and presence of salts

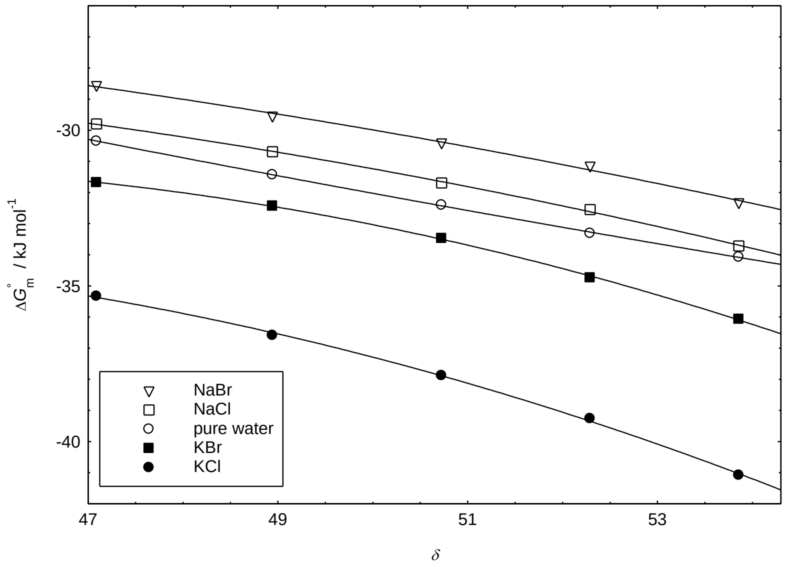

Figure. 4.35: $\Delta G^\circ_\mathrm{m}$ versus $\delta$for SDS in absence and presence of salts

4.4.3 Correlation of $\Delta G^\circ_\mathrm{m}$ with Solvophobic Parameter (S_p)

The solvophobic parameterS_p is calculated by Gibbs energies of transfer (Abraham *et al.*, 1988). We used the correlation method developed as in the literature (Wang *et al.*, 2011) and calculated the S_p values of the mixed solvents. It has been observed that water has high value of S_p=1 and 0.4 volume fraction of methanol has low value of S_p=0.698. A bigger S_p value mirrors the weaker interaction between hydrocarbon and solvent whereas a smaller S_p value has the stronger interaction between hydrocarbon and solvent.

The S_{p} values of hydrocarbon in methanol-water mixture affect the dissociation degree of SDS in the presence and absence of salts aggregate in the way that α values decrease with increasing S_{p}values(**Figure 4.36**). It can be seen from (**Figure 4.37**) that the $\Delta G_{\mathrm{m}}^{\circ}$values decrease with increasing S_{p} values in methanol-water solvent in presence and absence of salts. This indicates that the $\Delta G_{\mathrm{m}}^{\circ}$ values depend strongly on the solvophobic power of hydrocarbon in water-alcohol mixtures.

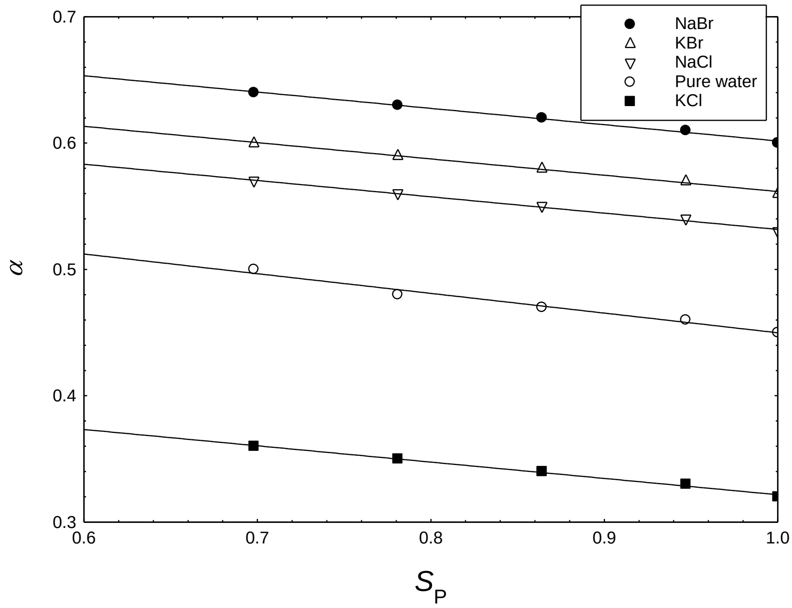

Figure. 4.36: α versus S_{p} for SDS in absence and presence of salts

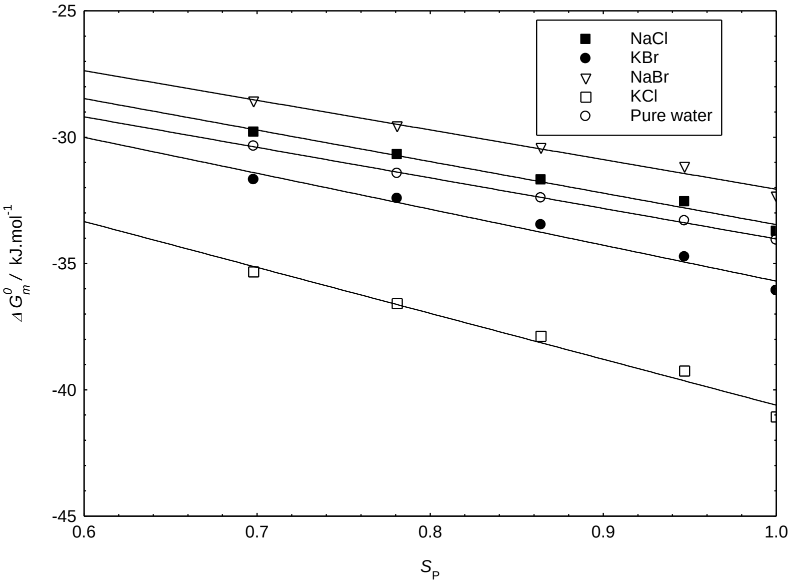

Figure. 4.37: $\Delta G_{\mathrm{m}}^{\circ}$ versus S_{p} for SDS in absence and presence of salts

4.5. Study of Surface Tension and Related Surface Properties of Sodiumdodecyl Sulphate

Due to the presence of the hydrophilic group with surfactant molecule prevents the surfactant being expelled completely from the solvent as a separate phase. It indicates that the reduction of the surface tension of water, is not only due to the amphiphatic structure of surfactant but it affects the orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented far from it. Due to this reason, they are called surfactants or surface active agents. Therefore, surfactant molecules are adsorbed at the interface in an oriented style. Generally, adsorption of surfactants occupies as single ions (Pan *et al.*, 2013) not as micelles. Adsorption of surfactant molecules have been studied to find (a) surfactant's concentration at the interface because this is a determination of amount of the interface has been covered by surfactant; the presentation of the surfactant in many interfacial processes (e.g. detergency, foaming, emulsification, etc) depends on its concentration at the interface: (b) the packing and orientation of the surfactant at the interface, because it finds how the interface will be affected by the adsorption, it means, whether it will become more hydrophobic or more hydrophilic: (c) the rate of adsorption at which this adsorption takes place, because this determines the routine in phenomena such as high-speed spreading or wetting and

Generally, surfactants show a regular decrease in surface tension with the increase in concentration and become the minimum then exhibits almost constant. The minimum concentration values of the surfactants are called critical micelle concentration.

The plot of the concentration versus surface tension of solution of SDS in pure water and in 0.10, 0.20, 0.30 and 0.40 volume fraction of methanol is used to find the cmc at 298.15, 308.15, 318.15 and 323.15 K. Typical experimental illustrations for determination of cmc by tensiometric method are illustrated in **Figures 4.38** to **4.41**.

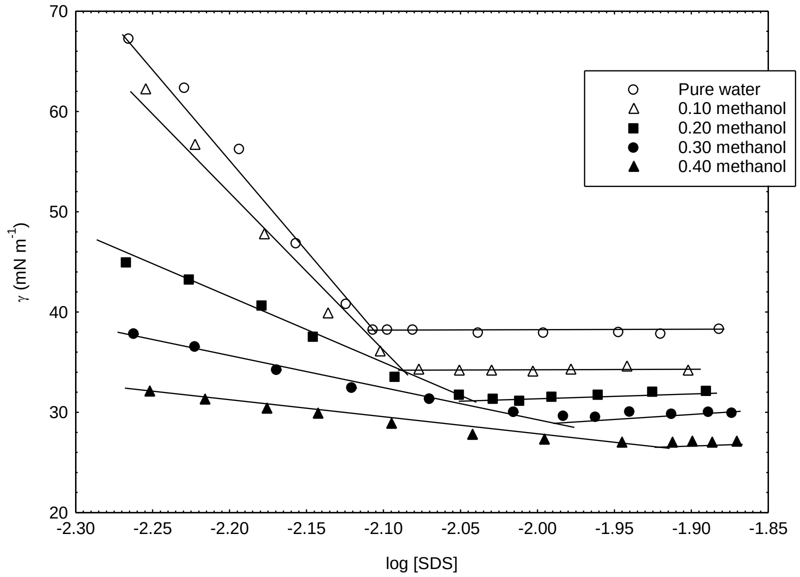

Figure 4.38: Plot of surface tension against concentration of SDS solution at 298.15 K, in pure water and in 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol

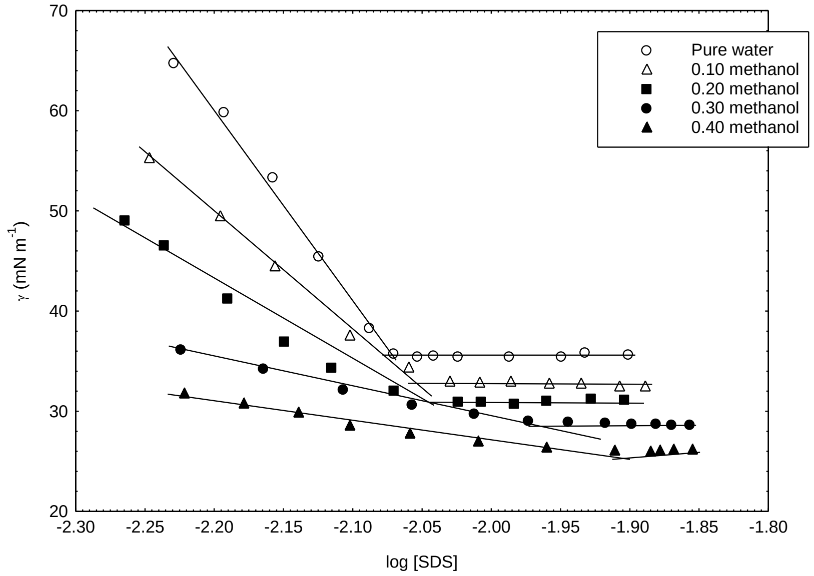

Figure 4.39: Plot of surface tension versus concentration of SDS solution at 308.15 K, in pure water and in 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol

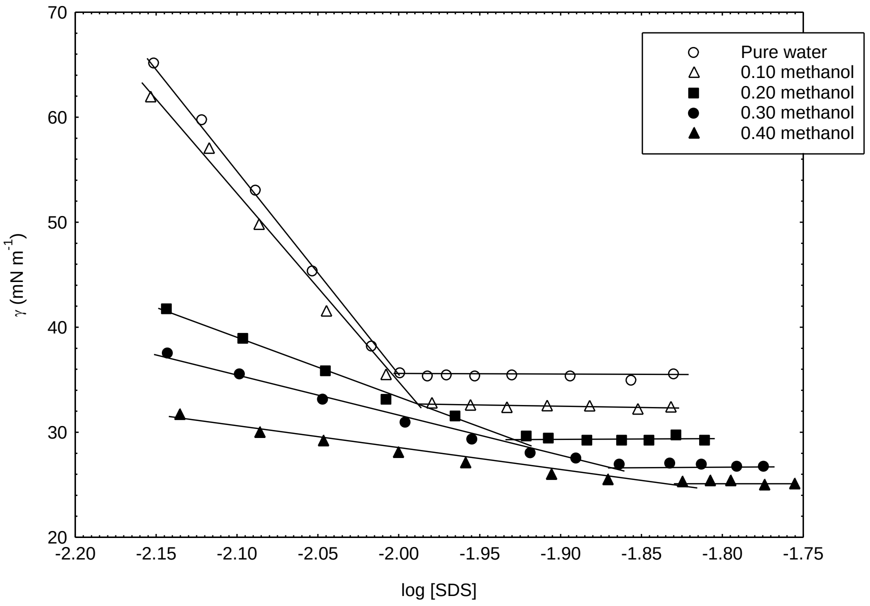

Figure 4.40: Plot of surface tension versus concentration of SDS solution at 318.15 K in pure water and in 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol

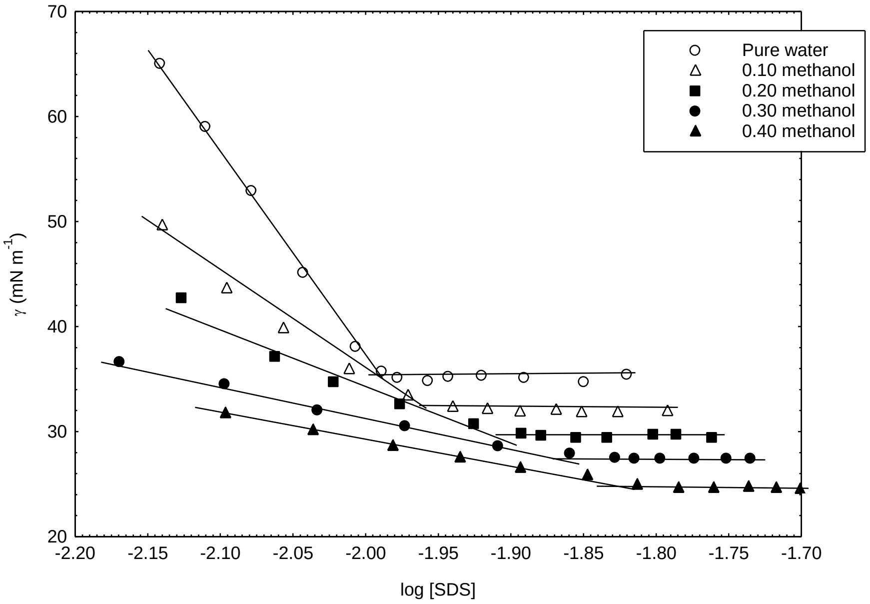

Figure 4.41: Plot of surface tension versus concentration of SDS solution at 323.15 K, in pure water and 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol

4.5.1. Surface Properties

Gibb's isotherm was used for the calculation of maximum surface excess concentration $\Gamma_{\max}$, at the air/methanol-water interface (Gibbs, 1928; Khatua *et al.*, 2004; Quagliotto *et al.*, 2003).

$$\Gamma_{\max} = -\frac{1}{2.303nRT}\left[\frac{d\gamma}{dlogC}\right]_{T,P} \quad \ldots\ldots\ldots\ldots\ldots \quad (4.13)$$

Here γ indicates the surface tension, R indicates universal gas constant, T indicates the absolute temperature and C indicates the concentration of surfactant. Here $(\frac{d\gamma}{dlogC})$ is the premicellar slope of the plot of γ versus log$C$ taken at cmc. For conventional surfactant where the surfactant ion and the counter ion are monovalent, the constant 'n' takes the value 2 (Alami *et al.*, 1993). The$A_{\min}$ (area occupied per surfactant molecule) at the air/methanol-water interface (Sugihara *et al.*, 2003) was determined by the relation:

$$A_{\min}=\frac{1}{N\Gamma_{max}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.14)$$

Here N is Avogadro's number.

The value of the π_{cmc} (surface pressure at the cmc) was found using following relation:

$$\pi_{\mathrm{cmc}}=\gamma_0 - \gamma_{\mathrm{cmc}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.15)$$

Hereγ_0 and $\gamma_{\mathrm{cmc}}$are the values of the surface tension of water and the surfactant solution at the cmc respectively. The $\Gamma_{\max}$ (surface excess concentration) is an effective measure of adsorption at air/water interface. It determines how much the air/solution interface has been changed by adsorption of surfactant and depends on the molecular structures of surfactants.

The small value of area occupied per surfactant molecule indicates that the orientation of the surfactant molecule at the interface is almost perpendicular (Israelachvili *et al.*, 1976).

The $\Delta G^{\circ}_{\mathrm{ads}}$ (standard free energy interfacial adsorption) at the air/saturated monolayer interface was calculated by the relation (Das and Das, 2009) given in equation 4.16.

$$\Delta G^{\circ}_{\mathrm{ads}} = \Delta G^{\circ}_{\mathrm{m}} - \frac{\pi_{\mathrm{cmc}}}{\Gamma_{\max}} \cdots\cdots\cdots\cdots\cdots (4.16)$$

The micellar shape is mainly governed by paking of surfactant and its geometry (Israelachvili *et al.*, 1976). The surface area of amphiphiles in mixed micelles and micellar growth (spherical-nonspherical) were used to find the packing parameters, *P:*

$$P = \frac{V_0}{A_{\min} l_{\mathrm{c}}} \cdots\cdots\cdots\cdots\cdots (4.17)$$

HereV_0 is the volume of exclusion per monomer in the aggregate, according to Tanford's formula (Tanford, 1980),

V_0 = (27.4+ 26.9n_c) Å^3, l_{c} = (1.54+1.26n_c) Å is the maximum chain length and n_{c} is the number of atoms of carbon in the chain of the hydrocarbon. *P* determines the geometry of micelles and indicates smallest sized aggregates in solution, which reduces the Gibbs free energy of micellization.

Study of the surface tension of surfactants in aqueous and mixed solvent media is applicable in different fields such as oil extraction, fire extinction, foams formation, etc (Jho, 1987). The surface tension of the surfactant solution is inversely proportional to the concentration of surfactant molecules in the system and at fixed concentration; the value of surface tension becomes almost constant as shown in **Figures 4.38 to 4.41**.

The values of cmc of SDS in water and in 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol are shown in Table 4.9 at 298.15, 308.15, 318.15 and 323.15 K. Change of slope i.e. $\frac{d\gamma}{dlog\mathrm{C}}$with volume fractions of methanol shown in **figure 4.42** indicates that methanol affect strongly the surface properties of surfactant solution as the slope is the major factor for the calculation of surface properties (Mukharjee *et al.*, 2013). $\Gamma_{\max}$, $A_{\min}$, π_{cmc},ΔG°_{ads} and P of SDS solutions in pure water, 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol at 298.15, 308.15, 318.15 and 323.15 K were calculated with the help of equations 4.13 to 4.17 and the values are displayed in Table 4.10. The calculated data showed that $\Gamma_{\max}$ as well as$\pi_{\mathrm{cmc}}$are inversely proportional to the volume fraction of methanol at particular temperature indicating the decrease in population of surfactant molecules at the interface with the addition of methanol. However, A_{min}values are directly proportional to the volume fraction of methanol. It indicates more area was occupied by surfactant molecule with the increase in methanol. P decreases with increase in volume fraction of methanol indicating loosely packing in increment of methanol.

The value of $\Delta G^{\circ}_{\text{ads}}$ is negative indicating the process of adsorption of surfactant molecules on the surface is spontaneous. The value of $\Delta G^{\circ}_{\text{ads}}$ becomes less negative with the addition of methanol at particular temperature indicates less spontaneity of adsorption of surfactant molecules on the surface. Such variations are also found in literature (Das *et al*., 2013; Harutyunyan, 2015; Manna and Panda, 2011; Pan *et al*., 2012). The cmc of SDS in pure water and 0.10, 0.20, 0.30 and 0.40 volume fraction of methanol measured with the help of surface tension are represented in Table 4.9 which have same trends as the data obtained by the calculation of conductance measurements.

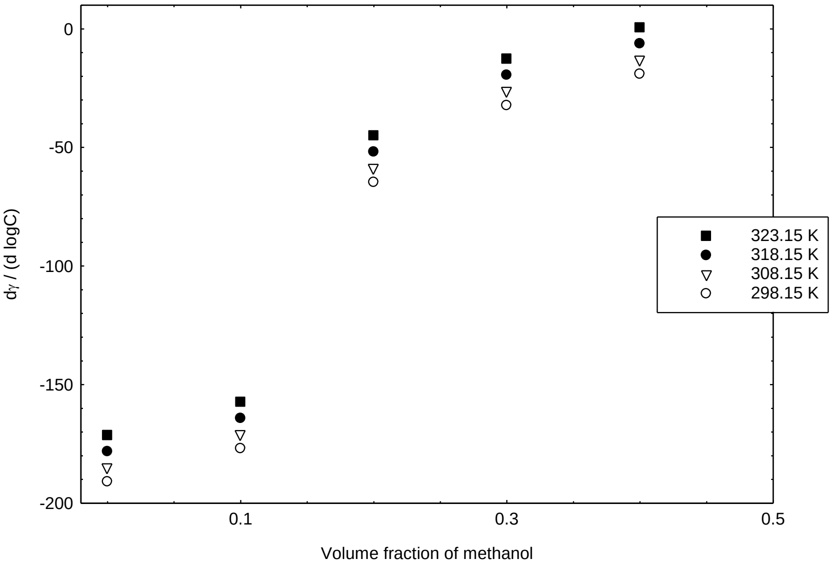

Figure 4.42: Variation of slope ($\frac{d\gamma}{dlogC}$) with volume fractions of methanol for SDS solutions

Table 4.9 CMC values of SDS by surface tension measurements in water, 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol at 298.15, 308.15, 318.15 and 323.15 K*

T / K	Volume fraction of methanol	cmc / mM
298.15	0.0	8.3
	0.1	9.2
	0.2	10.3
	0.3	11.7
	0.4	13.6
308.15	0.0	9.1
	0.1	10.3
	0.2	10.7
	0.3	13.1
	0.4	14.2
318.15	0.0	9.8
	0.1	10.7
	0.2	11.6
	0.3	13.7
	0.4	16.1
323.15	0.0	10.1
	0.1	11.8
	0.2	12.2
	0.3	13.9
	0.4	16.8

*The error limits of CMC are ±5%.

Table 4.10 Surface properties of SDS in water as well as in 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol at 298.15, 308.15, 318.15 and 323.15 K

T / K	Vol.fractions of methanol	$\Gamma_{\max}$ 10^6 (mol m^{-2})	$A_{\min}$ (A^2 $molecule^{-1}$)	π_{cmc} (mNm^{-1})	P	$\Delta G^{\circ}_{\mathrm{ads}}$ ($KJmol^{-1}$)
298.15	0.0	2.65	62.1	32.43	0.35	-46.311
	0.1	2.11	76.14	18.99	0.27	-42.3116
	0.2	1.45	112.54	12.03	0.17	-40.6958
	0.3	0.92	220.97	8.87	0.10	-40.069
	0.4	0.74	268.98	6.32	0.08	-38.8892
308.15	0.0	2.61	63.92	33.06	0.33	-45.9157
	0.1	2.01	92.72	17.59	0.25	-41.0022
	0.2	1.21	127.20	10.9	0.15	-40.2502
	0.3	0.61	261.67	5.55	0.07	-39.0269
	0.4	0.52	329.00	3.86	0.06	-36.2906
318.15	0.0	2.46	65.42	32.64	0.32	-45.7123
	0.1	1.79	98.10	19.32	0.23	-40.9924
	0.2	1.16	155.69	11.73	0.13	-40.014
	0.3	0.46	355.22	7.03	0.05	-39.0012
	0.4	0.37	440.72	4.06	0.04	-35.104
323.15	0.0	2.23	67.26	32.17	0.31	-45.3215
	0.1	1.76	102.55	20.25	0.22	-40.1324
	0.2	0.99	166.53	11.85	0.12	-39.9823
	0.3	0.39	417.16	6.99	0.04	-38.8731
	0.4	0.30	540.24	3.69	0.03	-34.3274

*The error limits of Γ_{max}, A_{min}, π_{cmc} and P are ±4, ±3, ±3 and ±5% respectively.

4.6. Study of Viscosity and Related Properties of Sodiumdodecyl Sulphate

The study of viscosity is highly useful to illustrate the real behavior of solute-solvent interaction which is very important to explain the properties of liquid crystal and microemulsion with respect to the micellar solution of the surfactant system.

There are two types of interactions in surfactant system. They are the interaction of solvent with solvophobic part and solvent with solvophilic part of the molecules of surfactant. Involvements of such interactions change the viscous flow of liquid which causes the variation of different physicochemical properties.

The plot of viscosity of SDS with the concentration in pure water, 0.10, 0.20, 0.30, and 0.40 volume fractions of methanol is shown in **Figure 4.43**. In this **Figure4.43**, it is seen that there is a break at a particular concentration known as critical micelle concentration.

The values of cmc of SDS in pure water, 0.10, 0.20, 0.30, and 0.40 volume fractions of methanol determined by measuring viscosity at 298.15, 308.15, 318.15 and 323.15 K are presented in Table 4.11. Below the cmc, the change of viscosity with variation in concentration was almost constant. Although above the cmc there is a remarkable change in viscosity with change in concentration as shown in **Figure 4.43**.

The linear variation of viscosity shows that the solute-solvent interaction is taking place with the increase in concentration. The increase in viscosity with the concentration of surfactant is explained due to increase in frictional force between solute and solvent molecules. At the fixed temperature, the viscosity of the solution increases on the addition of methanol. This phenomenon can be explained due to the decrease in average distance between surfactant and water molecules which results from stronger frictional force. The viscosity decreases with increase in temperature (**Figure 4.44**) because at the higher temperature, the kinetic energy of molecules increase which weakens the intermolecular force between liquid-liquid and liquid-solid on which liquid flow (Chandra *et al*., 2013).

The interaction between solvent and solute is described in terms of viscosity $'B'$ coefficient and given by Jones-Dole equation (Kay *et al*., 1966).

$$n_r = 1 + A\sqrt{C} + BC \quad \cdots\cdots\cdots\cdots\cdots\cdots (4.18)$$

Here $n_r = \frac{n}{n_0}$ is the relative viscosity of a solution, here A and B are constants. Equation 4.18 can be rearranged as equation 4.19.

$$\left(\frac{n_r - 1}{\sqrt{C}}\right) = A + B\sqrt{C} \cdots\cdots\cdots\cdots\cdots\cdots (4.19)$$

Here 'A' coefficient indicates the contribution from the interionic electrostatic force. The B coefficient indicates solute-solvent interaction. The plot of $\left(\frac{n_r - 1}{\sqrt{C}}\right)$ vs $\sqrt{C}$ for

SDS solutions in water, 0.10, 0.20, 0.30, and 0.40 volume fractions of methanol in post micellar region is presented in **Figures 4.45** at 298.15 K. The viscosityBcoefficients were determined from the slopes. The variations of 'β' values of SDS in water, 0.10, 0.20, 0.30, and 0.40 volume fractions of methanol at 298.15, 308.15, 318.15 and 323.15 K are presented in **Figure 4.46.**

From **Figure 4.46** shows that with the increase in temperature and on the addition of methanol there is the measurable influence on 'B' values. The 'B' values increase with the addition of methanol but decrease with increase in temperature. The first effect can be explained due to stronger solute and solvent interaction. The next effect is due to thermal expansion with increase in temperature. Addition of methanol makes the solvent more hydrophobic due to the decrease in relative permittivity which causes solubilization of micelle and the inter-molecular force between more hydrophobic solvent and tail of surfactant molecules increases. This makes less effective of intermolecular force and therefore solute-solvent interaction decreases which are indicated by lower 'B' values (Chandra *et al.*, 2013; Kay *et al.*, 1966; Tanaka *et al.*, 1973).

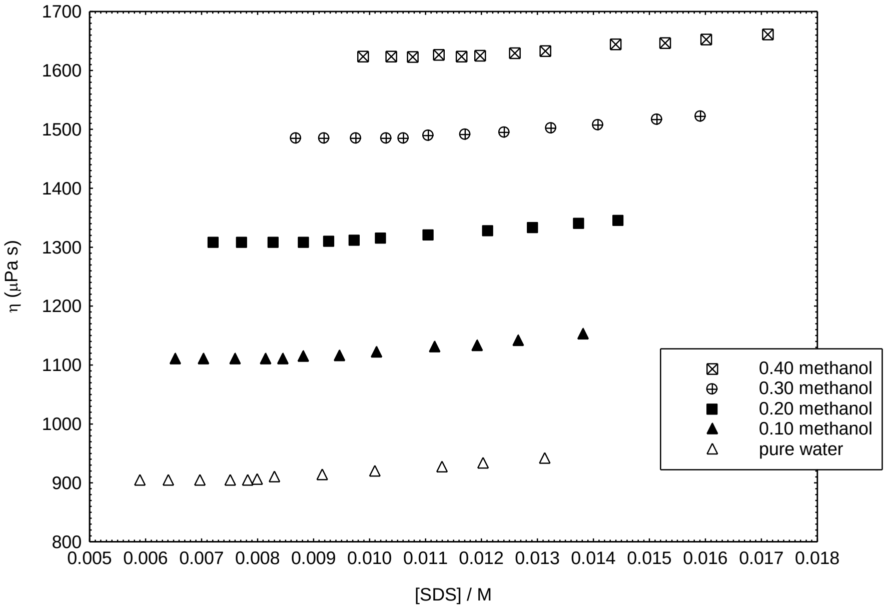

Figure 4.43: Plot of viscosity versus concentration of SDS solution at 298.15 K

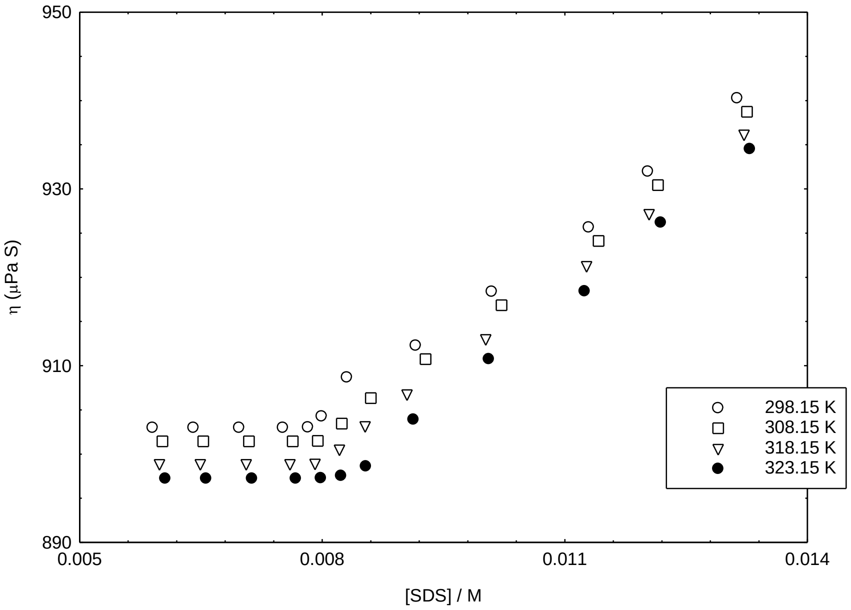

Figure 4.44: Plot of viscosity versus concentration of SDS in distilled water at four different temperatures

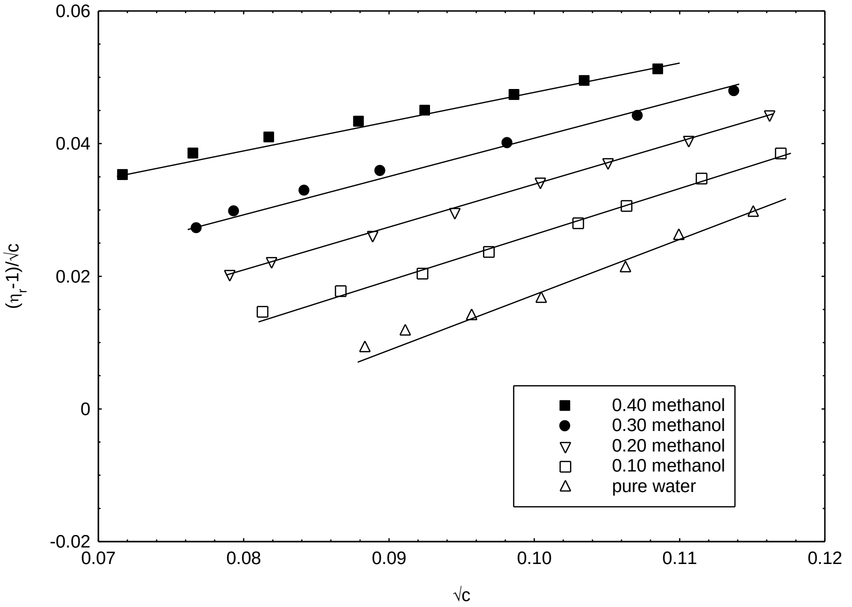

Figure 4.45: Plot of ($\frac{n_{r-1}}{\sqrt{C}}$) vs √C for SDS solution at 298.15 K

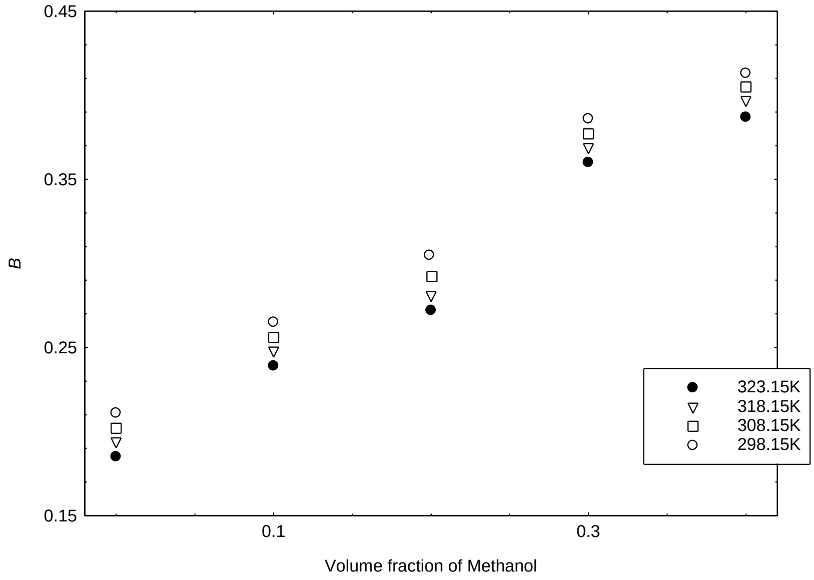

Figure 4.46: Variation of viscosity Bcoefficients of SDS solutions with volume fraction of methanol

Table 4.11 CMC values of SDS by viscosity measurements in water, 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol at 298.15, 308.15, 318.15 and 323.15 K

T/K	Volume fraction of methanol	cmc /mM
298.15	0.0	8.1
	0.1	8.7
	0.2	10.1
	0.3	11.1
	0.4	13.2
308.15	0.0	8.9
	0.1	10.5
	0.2	11.0
	0.3	13.4
	0.4	14.3
318.15	0.0	9.5
	0.1	10.8
	0.2	12.1
	0.3	13.9
	0.4	16.4
323.15	0.0	9.8
	0.1	11.9
	0.2	12.6
	0.3	14.2
	0.4	17.1

[*] The error limits of CMC are ±5%.

CHAPTER 5

5. CONCLUSIONS AND RECOMMENDATION

5.1. Conclusions

The study of density and partial molar volume showed that density is directly proportional to concentration but partial molar volumeremains almost constant at the fixed temperature. However, with the change in solvent composition by adding methanol, partial molar volumes, as well as densities, are decreased. It indicates that there is the presence of strong solute-solvent interactions. Temperature effect showed that with the increase in temperature the partial molar volume increased but densityis decreased.

Experimental results for the density of the salt-free solution of sodiumdodecyl sulphate in presence of cetyltrimethylammounium bromide in pure water and methanol-water mixed solvent media presented as a function of surfactant concentration and temperature.The densityis found to decrease with increasing temperature over the entire concentration range investigated in a given mixed solvent medium, whereas these values were also found to decrease as the relative permittivity of the medium decreased. With thehelp of density measurement, the calculated apparent molar volumes of SDS-CTAB presented as a function of surfactant concentration and temperature. The apparent molar volumes found to increase with increasing temperature over the entire concentration range investigated in a given mixed solvent medium. Furthermore, at a particular temperature, the apparent molar volumes found almost the same in the given concentration range of sodiumdodecyl sulphate in presence of cetyltrimethylammounium bromide and these values were found to decrease as the relative permittivity of the medium decreases.

The plot of specific conductivity versus concentration showed that there is remarkable break which indicates the morphological change in the solution in terms of aggregates called micelle. From datas of conductivity, the critical micelle concentration of SDS solution found and different thermodynamic properties such as standard enthalpy of micellization ($\Delta H_{\mathrm{m}}^{\circ}$), standard free energy of micellization ($\Delta G_{\mathrm{m}}^{\circ}$), standard entropy of micellizaiton ($\Delta S_{\mathrm{m}}^{\circ}$), standard free energy of transfer ($\Delta G_{\mathrm{trans}}^{\circ}$), heat capacity of micellisation ($\Delta_{\mathrm{m}} C_{\mathrm{p}}^{\circ}$), correlation of $\Delta G_{\mathrm{m}}^{\circ}$ with solvent and solvophobic parameter

(S_P), compensation temperature (T_c) and solute-solute interaction (σ) are calculated. Compensation temperature can be interpreted as a characteristic of solute-solute and solute-solvent interactions, i.e. proposed as a measure of the "desolvation" part of the process of micellization. The intercept σ characterizes the solute-solute interaction.

$\Delta G_{\mathrm{m}}^{\circ}$ values are found to be negative in all the cases for SDS indicating that micellization is spontaneous. However, the addition of methanol affects the $\Delta G_{\mathrm{m}}^{\circ}$values making less negative indicating that micellization is less favorable when relative permittivity of the solvent medium is decreased. The negative values of $\Delta H_{\mathrm{m}}^{\circ}$ indicate that micellization is exothermic and positive values of $\Delta S_{\mathrm{m}}^{\circ}$ indicate that micellization increases by the change of entropy. Values of $\Delta_{\mathrm{m}} C_{\mathrm{p}}^{\circ}$ are negative which indicates the self-association of amphiphiles.

From surface tension measurement, the critical micelle concentrations calculated and found that addition of methanol and increase of temperature greatly affects the surface tension and related surface properties such as standard free energy of adsorption ($\Delta G_{\mathrm{ads}}^{\circ}$), surface excess concentration (Γ_{max}), minimum surface area (A_{min}), surface pressure (π_{cmc}), packing parameter (P). Analysis of data showed that $\Delta G_{\mathrm{ads}}^{\circ}$ values are more negative than that of $\Delta G_{\mathrm{m}}^{\circ}$ which indicates that adsorption is more spontaneous than the formation of the micelle. With the increase in volume fraction of methanol, negative values of $\Delta G_{\mathrm{ads}}^{\circ}$ decreased, Γ_{max} decreased, A_{min} increased, (π_{cmc}) decreased and 'P' also decreased.

From viscosity measurement, B coefficient for SDS solutions pure water and in mixed solvent media of methanol-water mixture is estimated with the help of Jones-Dole equation. The values of B are highly affected by methanol content and temperature. Viscosity B coefficient describes the solute-solvent interaction. It indicated that addition of methanol makes the solvent more hydrophobic due to which it has stronger dragging tendency of solvent to the solute.

Addition of KCl, KBr, NaCl and NaBr decreases the micellisation of SDS due to the screening of the electrostatic repulsion of head groups. The calculation of different thermodynamic properties in presence of KCl, KBr, NaCl and NaBr such as standard enthalpy of micellization ($\Delta H_{\mathrm{m}}^{\circ}$), standard free energy of micellization ($\Delta G_{\mathrm{m}}^{\circ}$), standard entropy of micellizaiton ($\Delta S_{\mathrm{m}}^{\circ}$) and standard free energy of transfer ($\Delta G_{\mathrm{trans}}^{\circ}$) gave new findings in case of SDS with monovalent salts.

5.2. Recommendations

The study can be extended further to explore properties at the molecular level by using some sophisticated technologies such as SANS (Small Angle Neutron Scattering), DLS (Dynamic Light Scattering), NMR (Nuclear Magnetic Resonance), ITC (Internal Titration Calorimetry), Molecular modeling, etc. It can also extend by the study of osmotic pressure, equivalent conductance, etc to explore physiochemical properties of SDS as well as other surfactants.

CHAPTER 6

6. SUMMARY

The chapter ‘1’ contains introduction of the research work. It contains introduction about surfactants, definition, history, classification uses of surfactants, the condition of formation of micelle, critical micelle concentration and the equation of calculation of different thermodynamic properties like standard free energy, standard entropy and standard enthalpy of micellization, etc are included. The equation of calculation of surface properties like maximum surface excess concentration, area occupied per surfactant molecule, surface pressure at the cmc, packing parameters and equation for the calculation of B coefficient given by Jone-Dole equation are also mentioned. The general idea of the study of mixed surfactant (SDS-CTAB) is also here. In this chapter introduction of conductance, surface tension, viscosity, density and partial molar volume are mentioned and effect of these properties of sodiumdodecyl sulphate in aqueous solution and in the methanol-water mixture in four different volume fractions of methanol at four different temperatures are included. The conductance of SDS in pure water and four different volume fractions of methanol in presence and absence of four alkali metal halides are also included. Rational and objectives of the work are also included in this chapter.

In chapter ‘2’ literature review of the research work is included. Here literature, different works in SDS at various temperatures in the different solvent medium in absence and presence of various additives including salts and cationic surfactants are included.

The chapter ‘3’ contains information about chemicals, apparatus and methods used for this research work. It contains the method of preparation of different mixed solvents, mixed surfactants solution, method of measurement of conductance, surface tension, viscosity, and density by using Conductivity meter, Mansingh Survismeter and specific gravity bottle.

The chapter ‘4’ contains results and discussion of the research work. Density and partial molar volume of SDS and effect of temperature and addition of methanol on these properties are mentioned and density, apparent molar volume of CTAB and SDS are discussed. Different tables, **figures** containing conductance, critical micelle concentration, the standard free energy of micellization, the standard entropy of micellization, the standard enthalpy of micellization, the standard free energy of transfer, the heat capacity of micellization, the compensation temperature and solute-solute interaction parameter in different medium at different temperatures in absence as well as in presence of four alkali metal halides of SDS are shown in this chapter. The variations of the standard free energy of micellization with solvent parameters as Reichardt's parameter, Hildebrand parameter, Gordon parameter, relative permittivity at 298.15 K are mentioned. The variations of the standard free energy of micellization with solvophobic parameter and the variations of the solvophobic parameter with the degree of dissociation at 298.15 K are also included. The viscosity and its related properties, as well as surface tension and its surface properties, are presented.

The chapter '5' contains conclusions of the research work and recommendation for the further works.

In chapter '6' chapter wise summary of whole works are presented.

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APPENDIX

List of Research Papers Published/accepted in Journals

International Journals

1. Ajaya Bhattarai, Sujeet Kumar Chatterjee, Tulasi Prasad Niraula "Effects of concentration, temperature and solvent composition on density and apparent molar volume of the binary mixtures in cationic-anionic surfactants in methanol-water mixed solvent media'' *SpringerPlus, a springer open Journal,* 2, 280-288 (2013).

2. Tulasi Prasad Niraula, Sujit Kumar Shah, Sujeet Kumar Chatterjee, Ajaya Bhattarai"Effect of methanol on the surface tension and viscosity of sodiumdodecyl sulfate (SDS) in aqueous medium at 298.15 to 323.15 K"*Karbala International Journal of Modern Science,* in press.

3. Tulasi Prasad Niraula, Sujeet Kumar Chatterjee, Ajaya Bhattarai "Micellization of sodium dodecyl sulfate in presence and absence of alkali metal halides at different temperatures in water and methanol-water mixtures, *Journal of Molecular Liquids,* in press.

National Journals

1. Sujit Kumar Shah, Tulasi Prasad Niraula, Ajaya Bhattarai and Sujeet Kumar Chatterjee "A comparative study of critical micelle concentration (cmc) and free energy of micellisation ($\Delta G_{\mathrm{m}}^{0}$) of cationic surfactant (dodecyltrimethylammonium bromide, DTAB) and anionic surfactant (sodiumdodecyl sulphate, SDS) in different composition of methanol-water mixed solvent media by conductometric method at 308.15" *Bibechana, A Multidisciplinary Journal of Science, Technology and Mathematics*, 8, 37-45 (2012).

2. Tulasi Prasad Niraula, Sujeet Kumar Chatterjee and Ajaya Bhattarai, "Conductance of sodiumdodecyl sulphate in presence and in absence of KCl and NaBr in methanol-water mixed solvent media at 308.15 K". *Journal of Nepal Chemical Soc*iety, 29, 5-10 (2012).

3. Tulasi Prasad Niraula, Ajaya Bhattarai and Sujeet Kumar Chatterjee "Effects of concentration, relative permittivity on the transport properties of sodiumdodecyl sulphate in presence and in absence of potassium bromide and sodium chloride in

methanol-water mixed solvent media at 308.15 K''. *Bibechana,A Multidisciplinary Journal of Science, Technology and Mathematics*, 9, 159-164 (2013).

4. Tulasi Prasad Niraula, Ajaya Bhattarai, Sujeet Kumar Chatterjee "Sodiumdodecyl sulphate: A very useful surfactant for scientific investigations" *J. Knowledge and Innovation* vol. 2, No. 1, (111-113) (February 2014).
5. Tulasi Prasad Niraula, Sujeet Kumar Chatterjee, Ajaya Bhattarai " Effect of sodium chloride on the micellization of sodiumdodecyl sulphate in water and methanol-water systems" *Himalayan Journal of Science and Innovation* vol. 1, No. 1, (61-64) (July 2017).

Participation in Symposium and Seminars

1. Participated on "Workshop on research methodology", T.U. sponsored by Curriculum Development Centre and Research Center for Educational Innovation and development, T.U. Supported by Nepal University Teachers Association held at Biratnagar from October 2-4, 1994.
2. Paper presented on "The effect of soil paramerers for the corrosion behaviour of buried structural materials" in Eastern Region Chemical Symposium-2010, Biratnagar (May 14-15, 2010).
3. Participated on "Research methodology traning programme" 9th-15th July 2010, supported by University Grants Commission Nepal, held at Mahendra Morang Adarsh Multiple Campus, Biratnagar, Nepal.
4. Poster presented on "A conductometric study of sodiumdodecyl sulphate (SDS) in different composition of methanol-water mixed solvent media at 308.15 K, 318.15 K and 323.15 K" in Regional Chemistry Seminar 2011, Biratnagar May 7-8, 2011.
5. Poster presented on "A comparative study of critical micelle concentration (cmc) and free energy of micellization of cationic surfactants DTAB and anionic surfactant SDS in different composition of methanol–water mixed solvent media by conductometric method at 308.15 K" in the International conference on "Advanced Materials and Nanotechnology for sustainable development–October 21-23, 2011, Kathmandu, Nepal.
6. Poster presented on "Conductance of sodiumdodecyl sulphate (SDS) in presence and in absence of potassium chloride and and sodium bromide in methanol-water mixed solvent media at 308.15 K" in 6thNational Conference on Science and Technology (NAST) September 25th to 27th, 2012.
7. Paper presented on "Conductometric studies on the effect of NaBr on the micellisation of sodiumdodecyl sulphate (SDS) in pure water and methanol-water mixed solvent media at different temperatures" Seminar on Modern Trends in Science and Technology, (December 28-29, 2012) Biratnagar, Morang.
8. Participated on "Workshop on research writing and publishing" January 4, 2014, Biratnagar, Nepal.

9. Paper presented on "Study of critical micelle concentration of sodiumdodecyl sulphate in methanol-water mixed solvent media in presence and absence of monovalent salt by measuring surface tension and viscosity using Mansingh Survismeter" in International Conference on Emerging Trends in Science and Technology, (March 22-23, 2014), Biratnagar, Nepal.

10. Paper presented on "Critical micelle concentration of sodiumdodecyl sulphate in presence of monovalent salts at 318.15 K in pure water and methanol-water mixed solvent media with surface tension and viscosity methods" in Regional Chemistry Seminar August 30-31, 2014, Biratnagar, Nepal.

11. Paper presented on "Comparative study of critical micelle concentration of sodiumdodecyl sulphate in absence and presence of KCl and NaCl in pure water and in methanol-water mixed solvent media at 308.15 K by measuring surface tension and viscosity with Mansingh Survismeter on "International conference on Advanced Materials and Nanotechnology for sustainable development (November 4-6, 2014) Kathmandu, Nepal.

12. Participated on "Global Workshop on Recent Research Techniques" December 26th-27th, 2014, Biratnagar.

13. Paper presented on "A study of surface tension, viscosity and micellisation behavior of sodiumdodecyl sulphate in presence of monovalent salts (NaBr, KBr) in methanol-water mixed solvent media at 308.15 K and 318.15 K" in 1st National Conference on Chemical Sciences 9 January 2016 Organised by Nepal Chemical Society-Regional Committee, Butwal.

14. Paper presented on "Critical micelle concentration of sodiumdodecyl sulphate in presence and absence of NaCl, KCl, KBr and NaBr in pure water and in methanol-water mixed solvent media by conductometry at 323.15 K" in 7th "National Conference on Science and Technology" on 29-31 March, 2016.

15. Participated on "Training on communication skill development in scientific research" Organised by PG Campus Biratnagar, Morang on 6-8 July 2016.

16. Participated on "International workshop on research trends in synthesis, characterization and applications of new materials" 24th October 2016, Biratnagar, Nepal.

17. Paper presented on “Thermodynamics of Micelle Formation of Sodium Dodecyl Sulfate in presence and in absence of alkali metal halides at different temperatures in Pure water and methanol-water mixed solvent media” on 7th Asian Conference on Colloid and Interface Science (7th ACCIS) at Berjaya Times Square Hotel of Kuala Lumpur in 8-11 August, 2017 Organized by Asian Society for Colloidal and Surface Science.