SPECIFIC ION EFFECTS ON THE KRAFFT TEMPERATURE AND RELATED PHYSICO-CHEMICAL PROPERTIES OF TETRADECYLTRIMETHYLAMMONIUM BROMIDE

By

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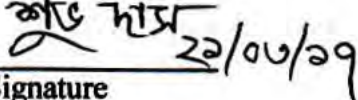
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DECLARATION

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

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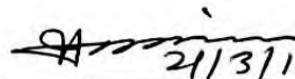   _____
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ABSTRACT

In the present work, the influence of some counterions on the Krafft temperature (T_K) and critical micelle concentration (CMC) of tetradecyltrimethylammonium bromide (TTAB) has been investigated. The thermodynamics of adsorption and bulk micellization as well as the solubilization of a water insoluble dye, sudan II in surfactant solution has also been investigated. It was found that the T_K of TTAB decreases in the presence of less chaotropic NO_3^- and Cl^- as well as kosmotropic SO_4^{2-} and to some extent F^- and increases in presence of more chaotropic SCN^-, I^- and to some extent Br^-. The order of ions in terms of decreasing the T_K is $NO_3^- > SO_4^{2-} > Cl^- > F^- > Br^- > SCN^- > I^-$. More chaotropic SCN^- and I^- form contact ion pairs with the surfactant cation, which results in the salting-out behavior with a consequent increase in the T_K. The activity of free water molecules increases in presence of less chaotropic NO_3^- and Cl^- and thereby hydration of TTAB molecules increases, showing a decrease in the T_K. Kosmotropic SO_4^{2-} and F^- having high charge density remain strongly hydrated in the bulk rather than forming contact ion pairs and thereby decrease the T_K. It was found that the CMC of TTAB decreases in presence of all the salts due to the screening of the micelle surface charge by the associated counterions with SO_4^{2-} being most effective in lowering the CMC and the propensity follows the order: $SO_4^{2-} > NO_3^- > Br^- > Cl^- > F^-$. The CMC of TTAB in pure water and in the presence of NaCl was found to increase gradually with increasing temperature. The thermodynamic parameters (changes in Gibbs free energy, enthalpy and entropy) for both adsorption and bulk micellization have also been calculated. The ΔG_m^0 and ΔG_{ad}^0 values are found to be negative which indicates that both the processes are spontaneous. For both adsorption and micellization the enthalpy and entropy terms are found to compensate with each other. The surface excess concentration (Γ) was found to decrease gradually with increasing temperature and the values are much higher in the presence of NaCl than the corresponding values in pure water. From the solubilization study it has been found that the CMC of TTAB decreases in presence of sudan II. It has also been found that the solubilization capacity in presence of NaCl is higher than that of pure TTAB.

Dedicated to my parents

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CHAPTER ONE
INTRODUCTION

1.1 SURFACTANTS AND THEIR TYPES

Surfactants (shorten for surface-active agents) are organic compounds containing in one molecule both lyophobic (hydrophobic) and lyophilic (hydrophilic) parts (Fig. 1.1). The lyophilic part of surfactants, also called "the head", has affinity to a polar solvent, while the lyophobic part ("the tail") has little or no attraction to that phase. Usually the solvent is water and then water soluble part is called hydrophilic. Water-insoluble group having affinity to nonpolar solvents, such as oils, is described as hydrophobic. The polar head groups content heteroatoms, such as oxygen, sulfur, phosphorus or nitrogen, included in functional groups of alcohols, esters, sulfates, amines etc. Nonpolar, hydrophobic tail consists of a hydrocarbon or fluorocarbon chain, linear or branched, containing usually 8-20 carbon atoms. Due to such amphiphilic structure, surfactants exhibit specific properties in solutions, as well as in solid state. When present at low concentrations in solutions they adsorb at all available interfaces (liquid/gas, liquid/liquid, liquid/solid) and as a consequence dramatically change their free energy. At higher concentrations, at and above the critical micellization concentration (CMC), when all the interfaces are occupied, surfactants self-assemble in the bulk in various aggregates: micelles, vesicles and liquid crystals. The type of formed supramolecular structure depends upon the structure and concentration of the surfactant, presence of the electrolyte, temperature, etc. [1, 2].

Figure 1.1: The basic structure of a surfactant

Surfactants are primarily classified on the basis of the charge of the polar head group. It is common to divide surfactants into the classes Anionics, cationics, nonionics and zwitterionics [3-6] as shown in the Figure 1.2
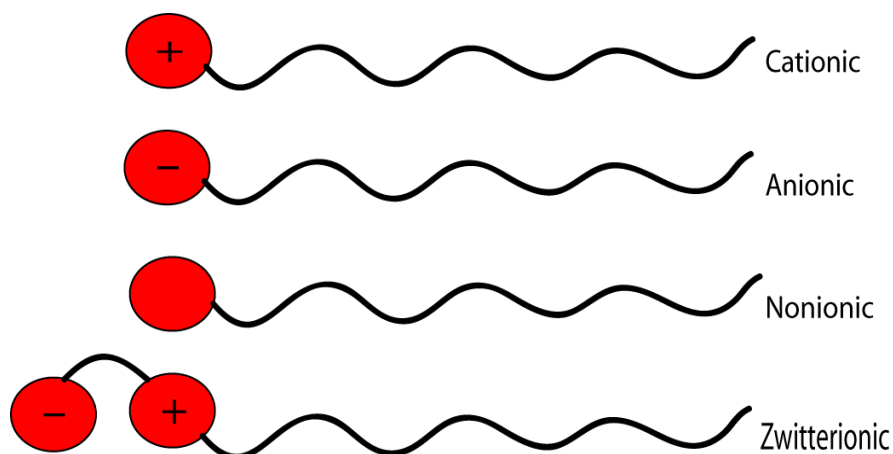
Figure 1.2: Four main types of surfactants

The ionic surfactants (Cationic or Anionic) have a net charge (positive or negative) located on the head group, whereas the nonionic surfactants have no net charge (neutral) but have polar head groups. Zwitterionic surfactants contain both a cationic and an anionic charge under normal conditions.

1.1.1 Anionic surfactants

Anionic surfactants are used in greater volume than any other surfactant class. One main reason of their greater usage is the ease and low cost of production. The hydroplilic part of the anionic surfactants can be a carboxylate, sulphate, sulphonate or phosphate. The most commonly used counterions are sodium, potassium, ammonium, calcium, and various protonated alkyl amines. Sodium and potassium impart water solubility, whereas calcium and magnesium promote oil solubility. Amine/alkanol amine salts give products with both oil and water solubility. They generally show sensitivity toward hard water.

Table 1.1: Representative examples of anionic surfactants

Surfactant	Molecular formula
Sodium dodecyl sulfate	$CH_3(CH_2)_{11}\text{-}SO_4^- Na^+$
Sodium stearate	$CH_3(CH_2)_{16}\text{-}COO^- Na^+$
Sodium dodecyl benzene sulphonate	$CH_3(CH_2)_{10}C_6H_4\text{-}SO_3^- Na^+$

1.1.2 Cationic surfactants

The vast majority of cationic surfactants are based on the nitrogen atom having the positive charge. Amine and quaternary ammonium-based products are common cationic surfactants. The amines function as a surfactant only in the protonated state, so they cannot be used at high pH. On the other hand, quaternary ammonium compounds are not pH sensitive. The usage of cationic surfactants is much lesser than that of anionic and nonionic surfactants. Their high expense is one of the main reasons of their less usage. The cationic surfactants which are hydrolytically stable show higher aquatic toxicity than most other surfactant classes.

Table 1.2: Representative examples of cationic surfactants

Surfactant	Molecular formula
Tetradecyltrimethylammonium bromide	$CH_3(CH_2)_{13}N^+(CH_3)_3Br^-$
Trimethyldodecylammonium chloride	$C_{12}H_{25}N^+(CH_3)_3Cl^-$
Laurylamine hydrochloride	$CH_3(CH_2)_{11}NH_3^+Cl^-$

1.1.3 Nonionic surfactants

Nonionic surfactants are the second largest surfactant class. They have either a polyether or a polyhydroxyl unit as the polar head group. The polar head group in the vast majority of nonionic surfactants is a polyether consisting of oxyethylene units, made by the polymerization of ethylene oxide. The typical number of oxyethylene units in the polar chain is five to ten, although some exceptions are also known where an extension in the number of oxyethylene units is observed e.g. dispersants. Polyhydroxyl (polyol)-based surfactants may also be ethoxylated. A common example is fatty acid esters of sorbitan and the corresponding ethoxylated products. Nonionic surfactants do not show any sensitivity toward hard water. The physicochemical properties of ethoxylated compounds are very much temperature dependent. At higher temperatures, they become more hydrophobic and less water soluble which is contrary to ionic compounds.

Table 1.3: Representative examples of nonionic surfactants

Surfactant	Molecular formula
Polyoxyethylene(4) dodecanol	$CH_3(CH_2)_{11}$-O-$(CH_2CH_2O)_4H$
Polyoxyethylene(9) hexadecanol	$CH_3(CH_2)_{15}$-O-$(CH_2CH_2O)_9H$
Alkylphenol ethoxylate	C_9H_{19}-C_6H_4-$(OCH_2CH_2)_nOH$

1.1.4 Zwitterionic surfactants

Zwitterionic surfactants have two charged groups of different sign. The positive charge is almost invariably ammonium, variation may occur in the source of negative charge, although carboxylate is by far the most common. They are often referred to as amphoterics, but the terms are not identical. On going from low to high pH, an amphoteric surfactant changes from net cationic via zwitterionic to net anionic. Neither the acid nor the base site is permanently changed, i.e. the compound is only zwitterionic over a certain pH range. Properties such as foaming, wetting, detergency etc are naturally affected by the change in charge with pH of the truly amphoteric surfactants, i.e. these properties will all depend strongly on solution pH. At the isoelectric point the physicochemical behavior often resembles that of nonionic surfactants. Below and above the isoelectric point there is a gradual shift towards the cationic and anionic character, respectively. They are the smallest surfactant class partly due to their high price. They show very low eye and skin irritation. They are therefore well suited for use in shampoos and other personal care products.

Table 1.4: Representative examples of zwitterionic surfactants

Surfactant	Molecular formula
Dodecyl betaine	$C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$
Dodecyldimethylammonium acetate	$CH_3(CH_2)_{11}(CH_3)_2 N^+CH_2COO^-$
Lauramidopropyl betaine	$C_{11}H_{23}CONH(CH_2)_3N^+(CH_3)_2CH_2COO^-$

1.2 PROPERTIES OF SURFACTANTS IN AQUEOUS SOLUTION

1.2.1 Adsorption of surfactants at air-water interface

When surfactant is present in a solvent, the lyophobic groups distort the structure of the bulk. Surfactants dissolved in aqueous phase breaks the hydrogen bonds between water molecules and structure them in the vicinity of the hydrophobic tails [7]. As a result, the free energy of the system increases. In order to minimize this unfavorable effect, molecules of amphiphile have to rearrange. Surfactant will diffuse and adsorb at the surface with its hydrocarbon tail oriented out of the water (Fig. 1.3). The presence of hydrophilic groups prevents the surfactant from being completely expelled from the solvent.
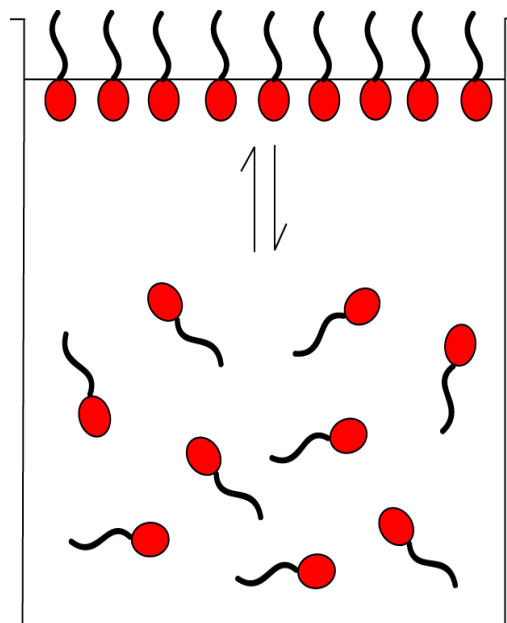
Figure 1.3: Adsorption of surfactants at the air-water interface

Adsorption of surfactant molecules lowers the interfacial tension and alters other properties of the interface, such as its charge and composition [1]. The denser is the layer of surfactant on the surface, the larger is the reduction of surface free energy. The amount of surfactants adsorption at the interface, as well as their efficiency in lowering the interfacial tension depends on their structure, concentration, conditions and the nature of phases forming the interface. For example, more surface active surfactants modify interfacial properties at lower concentrations. For nonionic surfactants repulsion between the head groups is small; therefore, they are usually strongly adsorbed at the surface from very dilute solutions and lower surface tension

much more than ionic surfactants with the same alkyl chain length. Moreover, the adsorption of nonionic surfactants is only slightly affected by addition of electrolytes or pH changes. For a given homologous series of straight-chain surfactants in water, efficiency of adsorption is directly related to the length of the hydrophobic chain, as shown in Fig. 1.3. If the temperature or composition of the solvent is changed, the effectiveness of surfactant may be significantly altered. That leads to a conclusion that amphiphile must possess desired properties in a certain solvent, and for the proposed conditions of use. An understanding of the surfactant science is necessary for choosing the best amphiphile for use in a particular system [2].

1.2.2 Critical micelle concentration

The physico-chemical properties of surfactants vary markedly above and below a specific surfactant concentration known as the critical micelle concentration (CMC) [1,2,8-10]. Below the CMC value, the physico-chemical properties of ionic surfactants (e.g., conductivities, electromotive force measurements) resemble those of a strong electrolyte. Above the CMC value, those properties change dramatically, indicating a highly cooperative association process is taking place. In fact, a large number of experimental observations can be summed up in a single statement: almost all physico-chemical properties versus concentration plots for a given surfactant-solvent system will show an abrupt change in slope in a narrow concentration range (the CMC value). This is shown in Fig. 1.4
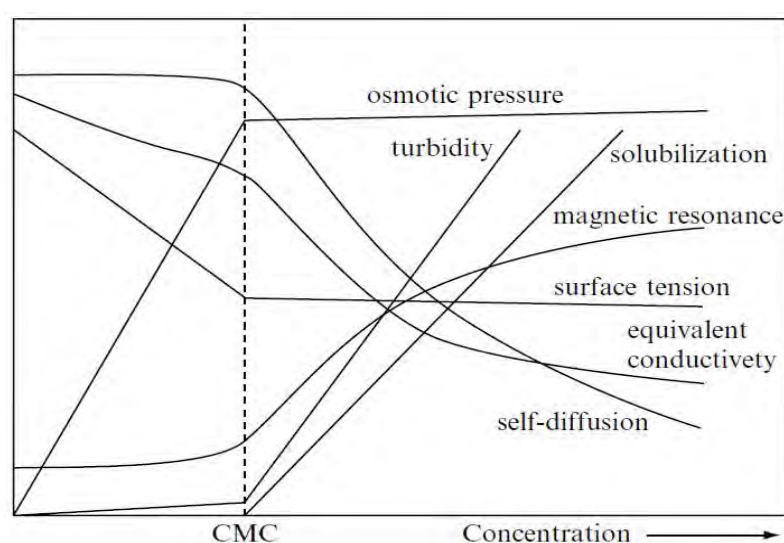
Figure 1.4: Variation in physical properties of surfactant solutions below and above the CMC value

In terms of micellar models, the CMC value has a precise definition in the pseudo-phase separation model, in which the micelles are treated as a separate phase and the CMC value is defined as the concentration of maximum solubility of the monomer in that particular solvent. The pseudo-phase model has a number of shortcomings; however, its description of the CMC value is very useful when discussing the association of surfactants into micelles. It is for this reason that the CMC value is, perhaps, the most frequently measured and discussed micellar parameter [11].

The CMC values are important in virtually all of the process industry surfactant applications, from mineral processing to formulation of personal care products and foods, to drug delivery systems, and to new surfactant remediation technologies. In these processes, surfactant must usually be present at a concentration higher than the CMC because the greatest effect of the surfactant, whether in interfacial tension lowering [12], emulsification, suspension stabilization, as a delivery vehicle, or in promoting foam stability [13] is achieved when a significant concentration of micelles is present. The CMC is also of interest because at concentrations above this value the adsorption of surfactant at interfaces usually increases very little. That is, the CMC frequently represents the solution concentration of surfactant from which nearly maximum adsorption occurs.

The general way of obtaining the CMC value of a surfactant micelle is to plot an appropriate physico-chemical property versus the surfactant concentration and observe the break in the plot.

The factors that affect the CMC in aqueous solution are given below: The length of the hydrophobic tail is a major factor to modify the CMC-value: for a homologous series of linear single-chain surfactants, the CMC decreases logarithmically with the carbon number. Furthermore, chain branching gives a higher CMC than a comparable straight chain surfactant [2]. For a given hydrophobic tail, the nature of the hydrophilic group is also of importance: varying the head-group from ionic to nonionic induces a strong decrease of the CMC-values (by one order of magnitude or more) since no electrostatic repulsion can oppose to micelle formation (driven by the hydrophobic effect). Varying the nature of conventional ionic groups, however, has only a less pronounced effect. Note that the intrinsic hydrophilicity of head-groups can be classified; for instance, among the common anionic hydrophilic groups the

usual ranking (starting from the less hydrophilic group) is the following: sulfate < sulfonate << carboxylate [14]. The nature of the counterion of ionic surfactants also influences the CMC. An increase in the degree of ion binding will decrease the CMC as the electrostatic repulsion between ionic groups will decrease. The presence of an added electrolyte also usually causes a decrease in the CMC of most surfactants (greatest effect for ionic ones). It allows to screen partially the electrostatic repulsion between head-groups and hence to lower the CMC. Finally, the influence of the temperature on micellization is generally weak for ionic surfactants (slight increase of CMC with T) while more important for nonionic surfactants (especially for ethylene oxide based surfactants) with a decrease of the CMC-value.

1.2.3 Micelle formation in aqueous solution

The physical properties of surfactant solutions differ from those of smaller or non amphiphilic molecules in a major aspect, namely the abrupt changes in their properties above a critical concentration, known as the critical micelle concentration (CMC) which is illustrated in Figure 1.4 with plots of several physical properties (osmotic pressure, solubilization, surface tension, conductivity, etc.) as a function of concentration of an ionic surfactant. At low concentrations, most properties are similar to those of simple electrolytes. One notable exception is the surface tension which decreases rapidly with increasing surfactant concentration. However, from a fairly sharply defined region, the properties exhibit sudden changes. This behavior results from the self-assembly of surfactant molecules in solution into so-called micelles.

Micelles are spontaneously formed clusters of surfactant molecules (typically 40 to 200), whose size and shape are governed by geometric and energetic considerations. They are loose, mostly spherical aggregates above their CMC in water or organic solvents [15]. Also, micellar aggregates are short-lived dynamic species, which rapidly disassemble and reassemble [16]. Hence, only average shape and aggregation numbers of micelles can be determined. Figure 1.5 represents a spherical micelle formed in aqueous solution, where the hydrophobic chains are directed towards the interior of the aggregate and the polar head-groups point towards water, hence allowing the solubility/stability of the aggregate (no phase separation). Micelles are also known to be disorganized assemblies whose interiors consist of mobile, non-

stretched hydrophobic chains [17]. It needs to be mentioned here that water molecules can penetrate partially the micelle core to interact with surfactant hydrophobic tails [18].
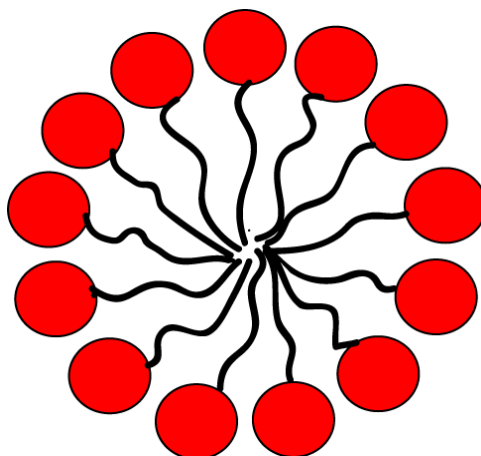
Figure 1.5: Scheme of a spherical micelle of surfactant monomers in aqueous solution

One of the most interesting properties of micellar aggregates is their ability to enhance the aqueous solubility of hydrophobic substances which are otherwise insoluble in water. The solubility enhancement originates from the fact that the micellar core can serve as compatible hydrophobic microenvironment for water-insoluble molecules. This phenomenon driven by hydrophobic interactions is referred to as solubilization [19]. It finds numerous applications such as for the environment friendly solubilization of organic solvents in water or for the design of drug delivery systems, or else in detergency.

Below the critical micellization concentration, surfactants adsorb at the surface of water, as shown in the previous section. At the CMC, the interface is at (near) maximum coverage and to minimize further free energy, molecules begin to aggregate in the bulk phase. Above the CMC, the system then consists of an adsorbed monolayer, free monomers and micellized surfactant in the bulk, with all these three states in equilibrium (Figure 1.6). Additional surfactants increase the micelle concentration or allow micelle growth, while the concentration of the unassociated monomers remains almost constant.
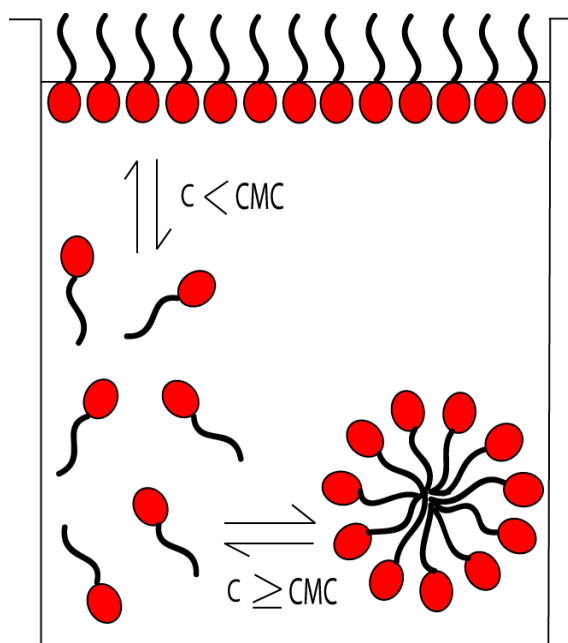
Figure 1.6: Schematic representation of the equilibrium in a surfactant solution above the CMC

The formation of micelles is a result of a complex interplay between hydrophobic forces and weak non directional repulsive forces. Hydrophobic forces which are opposed by electrostatic repulsion among the ionic head-groups at the micelle surface drive the micellization in water. This driving force is actually related to the formation of hydrophobic hydration shells around hydrophobic surfactant moieties. Traditionally, it was thought that water undergoes a structural enhancement in the hydrophobic hydration shell which is expressed in the formation of stronger and/or more hydrogen bonds per unit volume [20]. Upon aggregation these shells overlap and structured water is released. Thus, this process is accompanied by a gain in entropy. The current view is that water in hydrophobic hydration shells is not significantly more structured than that in the bulk [21-28]. It is widely accepted that water largely retains its original structure by accommodating the nonpolar solute in its hydrogen bonding network thereby maintaining as many hydrogen bonds as possible [21,28-30]. It has been argued that in order not to sacrifice hydrogen bonds compared to bulk water, the hydrogen bonds of water in the hydrophobic hydration shells adjacent to the apolar moieties are predominantly oriented tangentially to the apolar surface [21-24,29]. This leads to a loss of entropy due to a motion restriction of solvent molecules. At a certain surfactant concentration, the number of water molecules is not sufficient to form independent hydration shells, which results in

interferences and mutual obstructions of hydration shells (i.e. water molecules have to be part of two hydration shells simultaneously, which is highly unfavorable). As a result, the tendency to form aggregates increases rapidly [21]. Subsequently, the entropy lost upon formation of the tangentially oriented hydrogen bonds is regained upon aggregation since part of the water molecules surrounding the individual solutes is released. Hence, the micellization of surfactants is considered to be an entropy-driven process.

Although water is the primary solvent in surfactant studies and applications, aggregation behavior is not restricted to water and there are examples of the formation of aggregates in a wide variety of polar organic solvents of high cohesive energy density such as hydrazine, formamide, alkane diols (e. g. ethylene glycol) and ethyl ammonium nitrate [21,31], although the aggregate stability is generally lower than that in water [32]. In addition, the self-assembly is generally much less cooperative, the CMC much higher, and the micelles are smaller [2]. It is also notable that in apolar solvents the association is of low cooperativity and leads only to small and polydisperse aggregates. However, introduction of even small amounts of water can induce a cooperative self-assembly (via dipole-dipole interaction between the head-groups [33]), leading to reverse micelles.

1.3 THE KRAFFT TEMPERATURE

The solubilities of micelle-forming surfactants show a strong increase above a certain temperature, termed the Krafft temperature (Fig. 1.7). Below the Krafft temperture the solubility of the surfactant is too low for micellization. So, solubility alone determines the surfactant monomer concentration. Above the Krafft temperature a relatively large amount of surfactant can be dispersed in micelles and solubility increases greatly [34]. Above the Krafft temperature maximum reduction in surface or interfacial tension occurs at the CMC because the CMC then determines the surfactant monomer concentration. The Krafft temperature is defined as the temperature at which a rapid increase in the solubility of an ionic surfactant in water begins to appear due to the micelle formation [35]. On the basis of the (pseudo) phase model [36] the Krafft temperature is regarded as a triple point in the phase diagram of the surfactant/solvent system, at which a ternary equilibrium is established among the crystals, the micellar

surfactant, and the monomeric surfactant. According to the model of Hato and Shinoda [37] the Krafft temperature is the melting point of the hydrated solid.
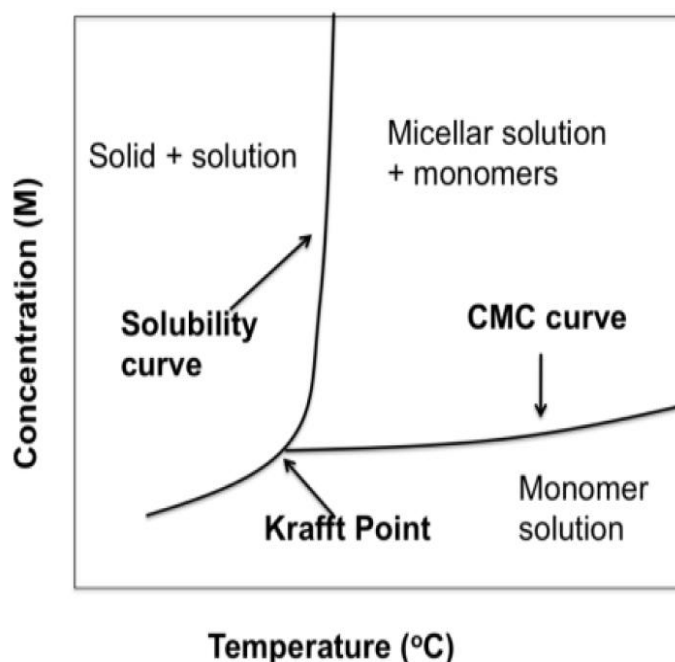
Figure 1.7: Schematic representation of the solubility curve for the ionic surfactants. The Krafft temperature (T_K) is the temperature at which surfactant solubility equals the CMC. Above T_K surfactant molecules form a dispersed phase; below T_K hydrated crystals are formed

1.4 THERMODYNAMICS OF MICELLIZATION

1.4.1 The pseudo-phase separation model

The pseudo-phase separation model suggests that the micelles form an independent phase, can be treated as a phase-separation phenomenon similar to vapor-liquid phase equilibrium of air-water system or to liquid-liquid phase equilibrium of aqueous-organic mixtures. The process of forming micelles as surfactant concentration reaches CMC is treated similarly to the formation of liquid droplets as the dew point pressure of a vapor is reached, as illustrated in Figure-1.8

As water molecules are added to an empty volume at constant temperature, the density of vapor phase (water molecules) increases steadily until the dew point pressure is reached. At the dew point, any added molecules would not contribute to the vapor density. The sharp transition at the dew point, as shown in figure, is very

similar to the transition at the CMC for surfactant solution forming large micelles, as shown in figure. Due to the near constancy of the free surfactant concentration above CMC, the surfactant solutions can be compared to a phase transition.
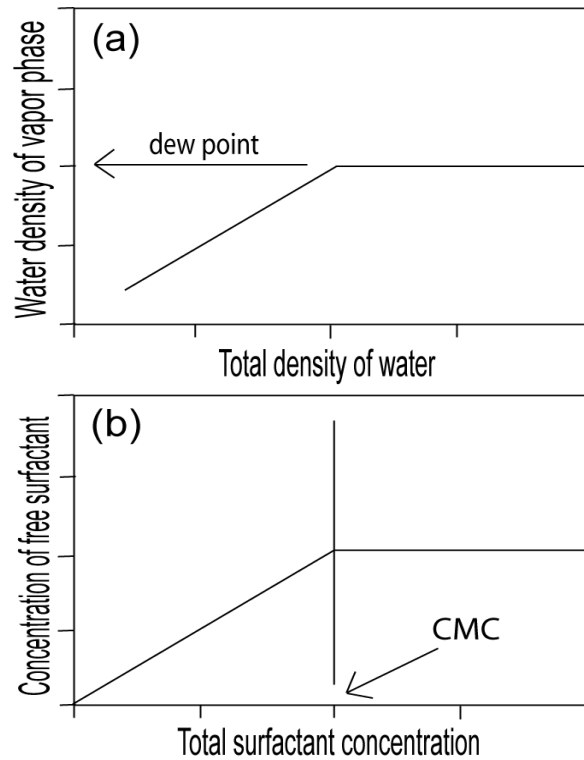
Figure 1.8: (a) Illustration of the liquid droplets formation (b) Illustration of the micelle formation

The method that has been proposed to give the expression of the pseudo-phase separation model can be described as:

The analogy method

Using the similarity of micelle formation to vapor-liquid equilibrium, an analogy method [38] is used to an equation of micelle formation. For a multi-component system at low pressures, the vapor-liquid equilibrium is described as

$$(y_i P)_{vapour} = (x_i \gamma_i P_i^0)_{liquid} \tag{1.1}$$

γ_i is the activity coefficient of component i in the liquid phase, P_i^0 and P are the vapor pressure of pure component i and the total system, respectively, x_i and y_i denote to the mole fraction of the liquid and vapor phase, respectively.

For a micelle-forming surfactant system, the analogy to equation (1.1) is

$$(y_i CMC)_{aq} = (x_i \gamma_i CMC_i^0)_{micelle} \tag{1.2}$$

γ_i is the activity coefficient of component i in the micelle pseudo-phase, CMC_i^0 is the critical micelle concentration of pure component i, CMC is the concentration of free surfactants (monomer) in the equilibrium with the micelles, i.e. the CMC of the mixed surfactant system, in analogy to the total pressure of vapour-liquid equilibrium system, x_i and y_i denote to the surfactant mole fraction in the micelle pseudo-phase and the bulk aqueous phase, respectively. The key assumption of this approach is that CMC has the same effects as the total pressure in a vapor-liquid equilibrium system.

1.4.2 The equilibrium model

The equilibrium model considers that the micellization process can be described by equilibrium between monomers, counterions, and monodisperse micelles. In the case of a cationic surfactant this equilibrium can be represented by [39]

$$nS^+ + (n-p)C^- \rightleftharpoons M^{p+} \tag{1.3}$$

The equilibrium constant for this equilibrium can be written as

$$K = \frac{[M^{p+}]}{[S^+]^n [C^-]^{(n-p)}}$$

Or, $lnK = ln[M^{p+}] - nln[S^+] - (n-p)ln[C^-]$

Or, $RTlnK = RT \left(ln[M^{p+}] - nln[S^+] - (n-p)ln[C^-]\right)$

Where S^+ represents the surfactant cations, C^- the corresponding counterions, and M^{p+} the micelle formed by n monomers with an effective charge of p. The standard free energy of micellization per mole of surfactant, ΔG_{mic}^o, is given by

$$\Delta G_{mic}^o = RT \left(-\frac{1}{n} ln a_{M^{p+}} + ln a_{S^+} + \left(1 - \frac{p}{n}\right) ln a_{C^-}\right) \tag{1.4}$$

Where a is the activity of the respective species. For large n values the first term of the parenthesis is negligible and both a_{S^+} and a_{C^-} can be replaced by the activity at the CMC. Moreover, since the micellar formation occurs in dilute solutions, the

activity can be replaced by the surfactant concentration (expressed in mole fraction) at the CMC. Considering these approximations, eq. (1.4) can be expressed as

$$\Delta G^o_{mic} = (2 - \beta)RTlnX_{CMC} \tag{1.5}$$

Where β ($\beta = p/n$) is the degree of counterion binding. The degree of counterion dissociation, α is related to β by the relation $\beta = (1-\alpha)$. By using this relation in equation (1.5) we get

$$\Delta G^o_{mic} = (1 + \alpha)RTlnX_{CMC} \tag{1.6}$$

Since the thermodynamic parameters are related by the Gibbs-Helmholtz equation, ΔG^o_{mic} can be separated into its enthalpic and entropic components as follows:

$$\Delta G^o_{mic} = \Delta H^o_{mic} - T\Delta S^o_{mic} \tag{1.7}$$

For the cases when the aggregation number and the degree of ionization are temperature dependent.

On the other hand, the entropy change of micellization, ΔS^o_{mic} is given by [40]

$$\Delta S^0_{mic} = -\left\{\frac{\partial(\Delta G^0_m)}{\partial T}\right\}_P \tag{1.8}$$

Since the thermodynamic parameters are related by the Gibbs-Helmholtz equation, ΔG^o_{mic} can be separated into its enthalpic and entropic components as follows:

$$\Delta G^o_{mic} = \Delta H^o_{mic} - T\Delta S^o_{mic} \tag{1.9}$$

Once ΔG^o_{mic} and ΔH^o_{mic} have been obtained, the entropy of micellization can be estimated from eq. (1.9)

The micellization is governed primarily by the entropy gain associated with it and the driving force for the process is the tendency of the lyophobic group of the surfactant to transfer from the solvent environment to the interior of the micelle [41].

The increased freedom of the hydrophobic chain in the nonpolar interior of the micelle compared to the aqueous environment plays an important role in entropy of micellization. Any structural or environmental factor that may affect the interaction between solvent-lyophobic group or interaction between the lyophobic groups in the

interior of the micelle, therefore, affect ΔG^o_{mic} and consequently the value of the CMC.

1.5 THERMODYNAMICS OF ADSORPTION

In order to provide a thermodynamic description of surfactant adsorption at the air-water interface, the physical quantity "surface excess" must be introduced. When considering a surfactant solution in equilibrium with vapor, the surface excess is defined as the concentration of surfactant molecules in a surface plane, relative to that at a similar plane in the bulk. This concept is central to the commonly used Gibbs treatment, which outlines the thermodynamic basis for variations in surface composition and surface tension. For a molecular system, it is reasonable to assume that the properties must vary with some function over the interfacial region from those of the pure liquid to those of the pure vapor and that an infinitely well resolved and abrupt discontinuity between the two is not physical.

Let us consider a system of bulk phases α and β and a surface phase σ, and make an approximation for the location of interface using the "Gibbs dividing surface". This is a plane that is chosen such that the excess adsorption of solvent is zero. In this plane, the excess adsorption, Γ^σ_i of a solution component i is then given by

$$\Gamma^\sigma_i = \frac{n^\sigma_i}{A} \tag{1.10}$$

Where A is the interfacial area. The term n^σ_i is the surface excess of component i in the surface phase σ compared with the bulk concentration if it had continued to the interface. The surface excess Γ^σ_i may be positive or negative, corresponding to surface enrichment or depletion of a solute, respectively.

The Gibbs adsorption equation is

$$d\gamma = -\sum_i \Gamma^\sigma_i \, d\mu_i \tag{1.11}$$

with γ the surface tension and μ the chemical potential. For a system consisting only of a solvent, 1, and a solute, 2, such as a nonionic surfactant dissolved in water, then equation (1.11) becomes

$$d\gamma = -\Gamma^\sigma_1 d\mu_1 - \Gamma^\sigma_2 d\mu_2 \tag{1.12}$$

The choice of the Gibbs dividing surface is such that $\Gamma_1^\sigma = 0$, then equation (1.12) simplifies to

$$dy = -\Gamma_2^\sigma d\mu_2 \tag{1.13}$$

Where Γ_2^σ is the solute surface excess concentration. At constant temperature, the chemical potential is given by

$$d\mu_i = const + RT d \ln a_i \tag{1.14}$$

Therefore, applying to equation (1.13) gives the common form of the Gibbs equation for nondissociating materials

$$dy = -\Gamma_2^\sigma RT d \ln a_2 \tag{1.15}$$

Or in rearranged form

$$\Gamma_2^\sigma = -\frac{1}{RT}\frac{dy}{d \ln a_2} \tag{1.16}$$

For dissociating solutes, such as ionic surfactants of the form R^-M^+, and assuming ideal behavior below the CMC, equation (1.16) becomes

$$dy = -\Gamma_R^\sigma d\mu_R - \Gamma_M^\sigma d\mu_M \tag{1.17}$$

For a system with no added electrolyte, the condition of electroneutrality at the interface requires $\Gamma_R^\sigma = \Gamma_M^\sigma$. Employing the mean ionic activities so that $a_2 = (a_R a_M)^{1/2}$ and substituting into equation (1.17) gives the Gibbs equation for 1:1 dissociating compounds:

$$\Gamma_2^\sigma = -\frac{1}{2RT}\frac{dy}{d \ln a_2} \tag{1.18}$$

If sufficient salt is added to screen out electrostatic effects, and the same counterion M^+ as the surfactant is present, then the activity of M^+ is constant and the prefactor becomes unity, so that the surfactant ion behaves as a nondissociating solute and equation (1.16) can be used. For dilute systems, concentration can be employed rather than activity in equations (1.16) and (1.18).

This equation directly tells us that when a solute adsorbs at the interface ($\Gamma_2^\sigma > 0$), the surface tension decreases with the increase of solute concentration. This is also known

as positive adsorption. Such a behavior is typical for weak or nonelectrolytes and surfactants in water, as shown in Fig. 1.9 (curves ii and iii). On the other hand, an increase in surface tension with the increase of solute concentration indicates that the solute avoids the interface ($\Gamma_2^\sigma < 0$). This is called negative adsorption and such a behavior is typical for strong electrolytes in water, as shown in Fig. 1.9 (curve i).
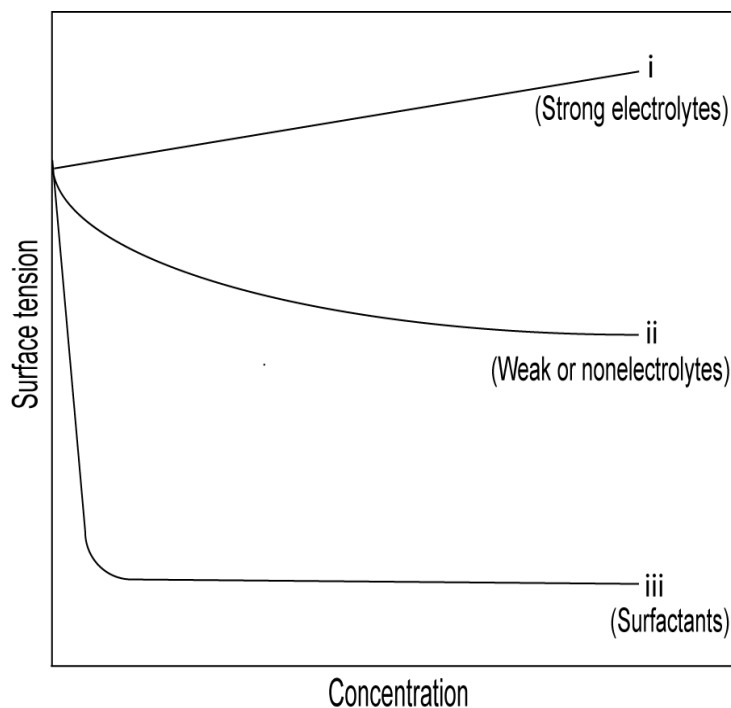
Figure 1.9: Dependence of surface tension of solutions on solute concentration

1.6 SOLUBILIZATION BY SURFACTANT SOLUTIONS

Solubilization is defined as the spontaneous dissolving of an insoluble substance in a solvent to form a thermodynamically stable isotropic solution with the help of surfactants [2]. In other words, a substance (e.g. hydrophobic compound) that is usually insoluble in a solvent (e.g. water) becomes soluble with the help of surfactants. Below the CMC of the surfactant, the solubility (amount of substance that is incorporated in the solution) is slightly higher than that in the pure solvent. However, just above the CMC, the solubility increases dramatically. And by adding even more surfactant, the solubility increases in a linear fashion, which can be seen in Figure 1.10. This is because micelles are formed which can accommodate the insoluble substance [42]. The higher is the concentration of surfactant (solubilizer),

the more solubilizate can be dissolved in the solution. The large solubilization capacity of the micelles towards nonpolar substances is caused by similarity of the micellar core to the corresponding alkane in a pure liquid oil. The solubilizing capacity of a surfactant is usually expressed quantitatively by a term known as molar solubilization ratio (MSR). The MSR can be defined as the number of moles of substance solubilized per mole of the surfactant in solution [43].
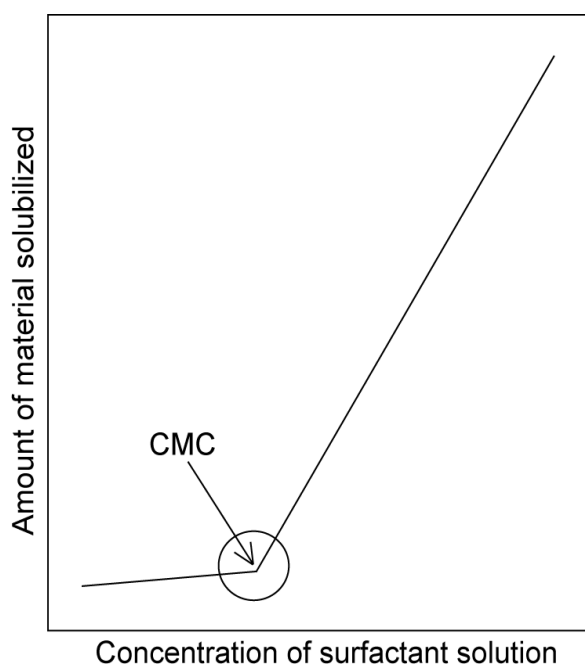
Figure 1.10: Amount of material solubilized as a function of concentration of surfactant solution

Solubilization is believed to occur at a number of different sites in the micelle: (1) on the surface of the micelle, at the micelle–solvent interface; (2) between the hydrophilic head groups (e.g., in POE materials); (3) in the so-called palisade layer of the micelle between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups that comprise the outer core of the micellar interior; (4) more deeply in the palisade layer; and (5) in the inner core of the micelle.
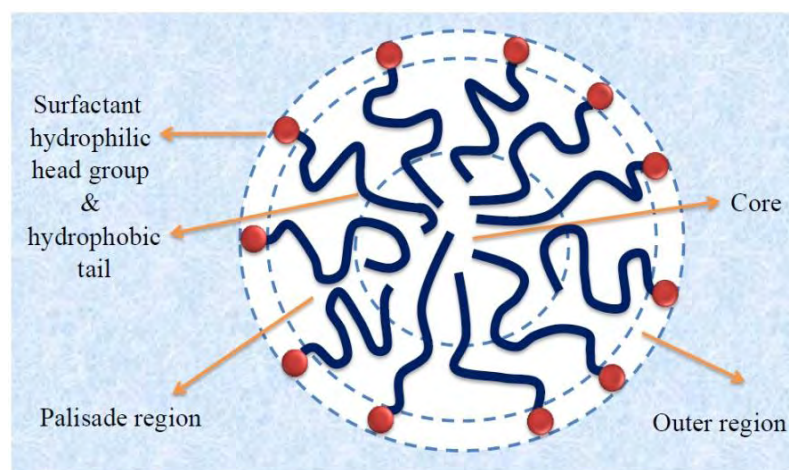
Figure 1.11: Different regions in the micelle on the basis of which different solubilization sites can be recognized

Solubilization into aqueous media is of major practical importance in such areas as the formulation of products containing water-insoluble ingredients, where it can replace the use of organic solvents or cosolvents; in detergency, where solubilization is believed to be one of the major mechanisms involved in the removal of oily soil; in micellar catalysis of organic reactions; in emulsion polymerization, where it appears to be an important factor in the initiation step; in the separation of materials for manufacturing or analytical purposes; and in enhanced oil recovery, where solubilization produces the ultralow interfacial tension required for mobilization of the oil. Solubilization into nonaqueous media is of major importance in dry cleaning. The solubilization of materials in biological systems (Florence, 1984) sheds light on the mechanisms of the interaction of drugs and other pharmaceutical materials with lipid bilayers and membranes. Separation processes based on micellar encapsulation [44-46] have a great importance in the removal of contaminants from groundwater and industrial wastewater. Bio-based ionic surfactants are added to contaminated reservoirs at concentrations above the CMC. The interior of the micelle will trap hydrocarbon wastes, while ionic contaminants can adsorb to the polar heads of the palisade layer. Later on, micelles can be removed using ultra filtration methods. Such a process is both cost effective and environmentally friendly.

1.6.1 Factors affecting the extent of solubilization

a) **Structure of the surfactant:** For hydrocarbons and long-chain polar compounds that are solubilized in the interior of the micelle or deep in the palisade layer, the amount of material solubilized generally increases with increasing the size of the micelles. An increase in the chain length of the hydrophobic portion of the surfactant increases the aggregation number and it results in an increase in the solubilization capacity for hydrocarbons in the interior of the micelle in aqueous media. Nonionic surfactants, because of their lower critical micelle concentrations, are better solubilizing agents than ionics in very dilute solutions. In general, the order of solubilizing power for hydrocarbons and polar compounds that are solubilized in the inner core appears to be as follows: nonionics > cationics > anionics for surfactants with the same hydrophobic chain length [47]. The greater solubilizing power of cationics, compared to anionics of equivalent hydrophobic chain length, may be due to looser packing of the surfactant molecules in the micelles of the former.

b) **Structure of the solubilizate:** For aliphatic and alkylaryl hydrocarbons, the extent of solubilization appears to decrease with increasing the chain length and to increase with unsaturation or cyclization if only one ring is formed. For condensed aromatic hydrocarbons the extent of solubilization appears to decrease with increase in the molecular size [48]. Short-chain alkylaryl hydrocarbons may be solubilized both at the micelle–water interface and in the core, with the proportion in the core increasing with increase in the concentration of the solubilizate. For polar solubilizates, the situation is complicated by the possibility of variation in the depth of penetration into the micelle as the structure of the solubilizate is changed. If the micelle is more or less spherical in shape, we can expect that space will become less available as the micelle is penetrated more deeply. Thus, polar compounds that are solubilized close to the micelle-water interface should be solubilized to a greater extent than nonpolar solubilizates that are located in the inner core. This is generally the case, if the surfactant concentration is not high. We should also expect that polar compounds that are solubilized more deeply in the palisade layer would be less soluble than those whose locus of solubilization is closer to the micelle–water interface. Usually, the less polar the solubilizate and

the longer its chain length, the smaller its degree of solubilization [49]; this may reflect its deeper penetration into the palisade layer.

c) **Effect of electrolytes:** The addition of neutral electrolyte to the ionic surfactant solution decreases the repulsion between the similarly charged head groups of ionic surfactant, thereby decreasing the CMC and increasing the aggregation number and volume of the micelles. The increase in aggregation number of the micelles presumably results in an increase in hydrocarbon solubilization in the inner core of the micelle. On the other hand, the decrease in mutual repulsion of the ionic head groups causes closer packing of the surfactant molecules in the palisade layer and a resulting decrease in the volume available there for solubilization of polar compounds [50].

d) **Effect of organic additives:** The hydrocarbon additive that is solubilized in the surfactant micelles causes the micelles to swell, and this may make it possible for the micelles to incorporate more polar material in the palisade layer. On the other hand, the solubilization of long chain polar organic additive into the micelles of a surfactant appears to increase the solubilization of hydrocarbons and the extent of solubilization increases with increasing the chain length of the polar compound [51]. The additives with longer chain length are solubilized more deeply in the interior of the micelle, and hence expand this region and thereby extent of solubilization increases.

e) **Effect of temperature:** For ionic surfactants, the extent of solubilization for both polar and nonpolar solubilizates increases with increasing temperature. An increase in temperature results in an increase in the thermal agitation which increases the space available for solubilization in the micelle [52]. For nonionic surfactants, the effect of temperature increase appears to depend on the nature of the solubilizate. Nonpolar materials which are solubilized in the inner core of the micelle, appear to show increased solubility as the temperature is raised. The solubility behavior of polar materials, whose locus of solubilization is the palisade layer of the micelle, appears to be very different, the amount of material solubilized generally going through a maximum as the temperature is increased to the cloud point. The increase in solubilization with increasing temperature up to the cloud point reflects the increase in thermal agitation of the surfactant molecules in the micelles. Further increase in temperature causes an increase in dehydration and thereby tighter coiling of the surfactant chains resulting in a

decrease in the space available in the palisade layer [2]. Therefore, amount of material solubilized decreases with further increase in temperature.

1.7 FIELDS OF APPLICATION OF SURFACTANTS

Surfactants are widely used and find a wide variety of applications because of their remarkable ability to influence the properties of surfaces and interfaces. There are two major areas of their use: consumer products and industrial uses. Industrial applications include the use of surfactants as cleaning agents and emulsifiers but their use stands out in the very important area of process aids. In the consumer product sector they are typically viewed as household cleaning agents and personal care products. Within the industrial area there is the industrial and institutional cleaning product sector, which mirrors many of the consumer applications. The other industrial use areas comprise product modifiers (concrete, drilling) or aids in manufacturing. Table 1.5 and Table 1.6 lists most of the applications of surfactants, but since these tend to be ubiquitous, one could never compile a complete list.

Table 1.5: Applications of surfactants in consumer products

Household cleaners	Personal care products

• Automatic dish detergents
• Fine fabric detergents
• Hard surface cleaners
• Light duty dish liquids
• Toilet soaps
• Scourers
• Heavy duty laundry detergents
  ➢ Powder and tablets
  ➢ Liquid
• Laundry aids
  ➢ Fabric softeners
  ➢ Bleach
• Specialty cleaners
  ➢ Rug cleaners
  ➢ Window cleaners
  ➢ Oven cleaners
  ➢ Metal polishes
  ➢ Toilet bowl cleaners
	• Bath and shower products
	• Cream rinse/conditioners
	• Hair preparations
	• Shampoo
	• Shaving creams
	• Skin creams and lotions
	• Toothpaste
	• Others
	  ➢ Aftershaves
	  ➢ Mouthwash
	  ➢ Denture cleaners
	  ➢ Nail polishes
	  ➢ Deodorants
	  ➢ Hair sprays
	  ➢ Hair dyes
	  ➢ Lipstick

Table 1.6: Applications of surfactants in commercial/industrial area

Industrial and institutional cleaners	Industrial processes

• Car wash products
• Carpet cleaners
• Commercial dishwashing
• Dairy and food plant cleaners
• Dry cleaning
• Electroplating baths
• Hard surface cleaners
• Industrial and institutional hand cleaners
• Industrial and institutional laundries
• Metal cleaners
• Printed circuit board cleaners
• Transport vehicle cleaners
• Agents
• Processing
• Foam
• Remediation
	• Agricultural chemicals
	• Asphalt
	• Corrosion inhibitors
	• Food and beverage
	• Dispersants
	• Metalworking fluids
	• Leather
	• Oilfield chemicals
	• Paint
	• Oil spill control
	• Ore flotation
	• Polishes
	• Petroleum additives
	• Slurries
	• Plastics and elastomers
	• Textiles
	• Wallboard
	• Miscellaneous
	  ➢ Adhesives
	  ➢ Sugar processing
	  ➢ Animal feed
	  ➢ Soil remediation
	  ➢ Fire extinguishing
	  ➢ Pharmaceutical
	  ➢ Polyurethane
	  ➢ foam
	  ➢ Mould release agents
	  ➢ Inks

Some specific fields of application of surfactants are discussed below:

1.7.1 Surfactants as detergents

Soap, a surface active fatty acid salt containing at least eight carbon atoms, [53] has long been used as a detergent. Soaps are excellent detergents, but suffer from their sensitivity to acid pHs and the presence of hardness in the water (Ca^{2+} and Mg^{2+} ions), causing soap scum. Although the use of detergent builders will compensate for this deficiency, soaps have been essentially replaced by the synthetic detergents. Not all surfactants make acceptable detergents. For a surfactant to be considered a good detergent, it must be a good wetting agent, possess the ability to displace soil

materials into the washing fluid, be a good solubilizing agent, and be a reasonable anti deposition agent. The solid surface to be cleaned may be a hard surface (plates, high density plastics, teeth) or a textile material (e.g. wool, cotton, synthetic fibres), or a part of the body (skin, hair, teeth). Surfactants that effectively adsorb at the solid/water and dirt/water interfaces make the best detergents. The most successful detergents are those forming micelles; hence, micelles were long thought to be an intimate part of the detergency mechanism. The chemical properties of surfactant molecules that are associated with good detergent action, will in most cases, lead to micelle formation as a competing process. The complete efficiency of detergents in practical situations is achieved by adding additives. Common additives include builders, anti-redeposition agents, brighteners, and co-surfactants.

1.7.2 Surfactants in health and personal care products

Quaternary ammonium surfactants (quats) have potent germicidal activity in addition to their use as fabric softeners in detergents. The best known fabric softener and antistatic agent is ditallow dimethyl ammonium chloride (DTDMAC). The popularity of "natural" cosmetics stems from the perception of better purity, safety and efficacy. Formulating a shampoo generally meets the following criteria: mild detergency, good foaming, good conditioning, adequately preserved and aesthetically appealing [54]. Cosmetic formulations are dependent on new formulation techniques for emulsions, particularly for storage properties [55]. The phase inversion temperature (PIT) emulsion and microemulsion are characterized by fine droplet sizes which are highly stable; microemulsions are useful for creating a clear formulation of O/W and also appear to create a less irritating product [56]. In a PIT system, the water/oil emulsion is cooled below the inversion range temperature, yielding an oil/water emulsion which generally has droplet sizes less than 200 nm, resulting in high kinetic stability. This formulation technique has found use in deodorant emulsion preparation [50]. Microemulsions may also be formed directly, but they are only stable over a limited temperature range. Stabilizers in form of new surfactants (e.g., alkyl polyglyosides) may extend the stability range over increased temperature ranges.

1.7.3 Surfactants in crop protection

Crop protection products refer to pesticides, herbicides, fungicides and insecticides. The current trend in crop protection is towards products that are more potent, safer to

user, having less impact on the environment, more convenient to use and improved efficiency of the applied product. In the case of sprayed products, colloid and interface science impacts all aspects of application. Surfactants are used as emulsifiers in spray preparations. Typical surfactants used in pesticide formulations are ethoxylated alcohols, alkyl phenols, sorbitan and alkylamines [57]. Organosilicone surfactants have begun appearing in commercial spray-application products [57]. They easily break down, which is an environmental bonus, but the lack of stability poses difficulty in product storage as ready-to-use products.

1.7.4 Surfactants in paper and cellulose products

Surfactants find its valuable usage in the paper making industry. They are used to prepare several components of paper such as pigments for producing white or colored paper and sizing agents, often emulsion polymers that bind the cellulose fibers in the finished product and incorporate strength and dimensional stability. Addition of proper surfactants often controls the water absorbing capacity of paper. One of the most important applications of surfactants in paper industry is in the process of recycling paper. A major step in the process is the removal of the ink and pigments present (deinking). That process which is also called flotation process in which a surfactant is used to remove substances adhering to the paper.

1.7.5 Surfactants in mining and flotation

Surfactants are applied with calcium chloride pastes which are used as preventor for coal dust explosions and as dust binding agents for mineral dust in mining operations. The function of surfactants in this case is to improve the wettability of the pastes. In the separation of raw material minerals, differences in surface properties of individual mineral species are being used. In the suspension of finely milled ore in water, air is sparged into the suspension. Minerals of value should float upwards by attachment to the air bubbles and thus be separated from the accompanying burden. The surface of the valuable mineral particles has to be hydrophobic to affect their attachment to the air bubbles and surfactant works here actively.

1.7.6 Surfactants in foods

Surfactants are involved in the production of many common food items and can be found in the extraction of cholesterol, solubilization of oils, liquor emulsification,

prevention of component separation, and solubilization of essential nutrients. One popular example of application of surfactants in foods is in the formulation of ice cream. Surfactants are a key component in the manufacture of edible coatings. A finish coat or polish may be added to chocolate- and sugar-panned confectionery products to produce an aesthetically pleasing gloss. Surfactants are added to create a dispersion of the coating particles, which then allows for proper wetting and adhesion over the candy surface. Surfactants are also used in the production of margarine.

1.7.7 Surfactants in textiles and fibers

In the manufacture and further processing of textiles, surfactants have a role as auxiliaries in a number of process steps. In pretreating of textile material, natural fibers are freed of accompanying substances (waxes, fats, pectines, seedhulls and other impurities). The detergents and wetting agents needed for this are primarily mixtures of different surfactant types. In the manufacture of textiles, surfactants are applied to optimize individual processing steps (drawing, spinning, twisting, texturizing, coning, weaving, knitting, etc).

1.7.8 Surfactants in biological systems

The understanding of the pulmonary surfactant system, has only been applied clinically since about 1990 for the treatment of respiratory distress syndrome. Surfactant replacement therapy may also be used in treating other forms of lung disease, such as meconium aspiration syndrome, neonatal pneumonia and congenital diaphragmatic hernia [58]. The lung surfactant system may also protect the lung from injury and infection caused by inhalation of particles and micro-organisms [58,59]. The formulation ingredients of therapeutic drugs include amphiphilic molecules and polymers. Polymeric micelles have emerged as drug delivery carriers for poorly water soluble drugs because they can solubilize the active component in their inner core, protecting it from contact with the surrounding aqueous environment. The micelle shell provides stabilization in the aqueous environment and interacts with plasmatic proteins and cell membranes. Other drug-delivery systems may include double emulsions, usually W/O/W, for transporting hydrophilic drugs such as vaccines, vitamins, enzymes, and hormones [60]. The multiple emulsion also allows for slow release of the delivered drug and the time release mechanism can be varied by

adjusting the emulsion stability. Conversely, in detoxification (overdose) treatments, the active substance migrates from the outside to the inner phase.

1.7.9 Surfactants in leather and furs

An important field of application of surfactants is in the manufacture of leather and furs, starting with the original untreated skin or hide and ending with the finished product. In leather tanning, the leather is treated with a surfactant to produce a protective coating on the skin and hide fibers. This helps prevent the fibers from sticking together and keeps the fiber network flexible or supple while increasing the tensile strength of the finished leather product. Surfactants may also help the penetration of dyes and other components into the fiber network thereby improving the efficiency of various stages of the tanning process, saving time, energy, and materials while helping to guarantee a higher-quality, more uniform finished product. The final surface finish of leather goods is now commonly applied in the form of lacquer like polymer coatings that can be applied as emulsions and suspensions, using suitable surfactants, of course. Surfactants have their similar applications in the fur industry.

1.7.10 Surfactants in pharmaceuticals

Surfactants are used in pharmaceutical industries in various ways. They are important as formulation aids for the delivery of active ingredients in the form of solutions, emulsions, dispersions, gel capsules, or tablets. They are also important in the preparations of time-release medications and transdermal dosification. But the important criteria that must be evaluated for their application in pharmaceuticals are biocompatibility, low toxicity and also proper emulsifying properties.

1.7.11 Surfactants in chemical industry

The chemical processes utilize the wetting and dispersing power of surfactants in processing. The systems which contain immiscible components, the reaction speed may be increased by the emulsification effect of surfactants, e.g., in splitting of fats by the Twitchell process, in hydrolytic splitting of wool wax and in hydrolysis of polyvinyl acetate. It is also necessary to mention phenol manufacture by the cumene process, preparation of ethylene carbamates and chlorination reactions. Surfactants may also be used to increase the yield in extraction processes.

1.8 SPECIFIC ION EFFECTS AND THE HOFMEISTER SERIES

Specific ion effects are ubiquitous in chemistry and biology. Such effects exhibit a reoccurring trend called the Hofmeister series [61,62], which is generally more pronounced for anions than for cations. The series was discovered in 1888 by Franz Hofmeister whereby it was shown that ions had consistent effects on the solubility of proteins. Recently, substantial attention has been paid to Hofmeister phenomena because of their relevance to a broad range of fields. Particular examples include protein stability [63,64], enzyme activity [65-68], protein-protein interactions [69,70], protein crystallization [71], optical rotation of sugars and amino acids [72], bacterial growth [73], the surface tension of aqueous interfaces [74,75], micelle formation [76-78], membrane permeability [79] and the phase behavior of monolayers and macromolecules [80-83]. The typical ordering of the anion series and some of its related properties are shown in Figure 1.12.

Hofmeister series of anions

Chaotropic behavior increases →

CO_3^{2-} SO_4^{2-} $H_2PO_4^-$ F^- Cl^- Br^- NO_3^- I^- ClO_4^- SCN^-

← Kosmotropic behavior increases

Kosmotropes		Chaotropes	
↑	Surface tension	Surface tension	↓
↓	Protein solubility	Protein solubility	↑
↓	Protein denaturation	Protein denaturation	↑
↑	Protein stability	Protein stability	↓
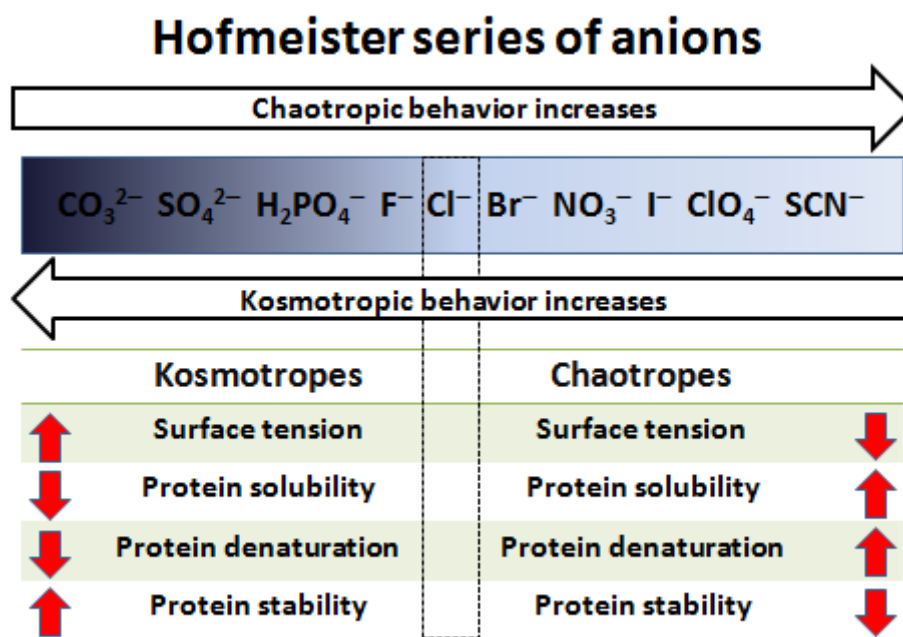
Figure 1.12: Schematic illustration of the Hofmeister series

The anions to the left of Cl^- are referred to as kosmotropes, while those to its right are called chaotropes. Cl^- is often considered to be the dividing line between chaotropic and kosmotropic behavior. The kosmotropes are strongly hydrated, salt proteins out of solution and prevent proteins from unfolding. On the other hand, chaotropes are weakly hydrated, salt proteins into solution and cause them to denature.

Traditionally, it was believed that Hofmeister ordering should be caused by changes in the hydrogen-bonding network of water in bulk solution [84]. Specifically, kosmotropes were thought to be water structure makers that strengthen aqueous hydrogen bonding, while chaotropes were believed to act as water structure breakers. However, recent experimental [85-89] and theoretical [90-92] investigations have cast serious doubt on this notion. In fact, it has been clearly demonstrated that bulk water structure making and breaking by salts is not central to the ion specific nature of most physical phenomena in solution. This led to the hypothesis that the Hofmeister series results from interfacial phenomena which involve the direct interaction of ions with the macromolecule/aqueous interface [93,94].

1.9 AIMS AND OBJECTIVES OF THE PRESENT STUDY

Surfactants are widely used in a variety of fields because of their profound influence on the properties of surfaces and interfaces. The fields of application of surfactants include food processing, enhanced oil recovery, agrochemicals, pharmaceuticals, personal care and laundry products, mineral processing, fuel additives, lubricants, paints, leather and furs, plastics and composite materials, coatings and adhesives. Surfactants are also applied in petroleum industries, textile industries, soil remediation techniques and other environmental issues [95]. One of the reasons for potential applications of surfactants is their ability to lower the surface or interfacial tension and form micellar aggregates when the surfactant concentration attains a definite value known as the critical micelle concentration (CMC). The effectiveness of surfactants is usually governed by their maximum lowering of surface tension and ease of micelle formation in the bulk [95]. Below the CMC, there is no possibility of micelle formation and surfactant molecules exist as monomers. Under this condition, the surfactant solution has only little or no influence on the solubility of nonpolar organic compounds. Micellar solutions have the special characteristics of solubilizing compounds that are otherwise insoluble in water [2,3]. Studies on the solubilization of water insoluble compounds in the micellar system have revealed a lot of applications of surfactants such as drug carrier, drug solubilization, toxic waste removal etc [96-99]. Although surfactants have found extensive applications in a wide range of fields, they do not work effectively below a certain critical temperature known as the krafft

temperature (T_K). The T_K is generally interpreted as the melting temperature of hydrated solid surfactants [2,100-104] and is known as the temperature above which an abrupt change in solubility of ionic surfactants occurs. Below the T_K, the solubility of the surfactant in aqueous system is very limited because of their existence in solution only in the form of monomers. Under such circumstances, both industrial and household applications become very limited as surfactants lose their dispersing, emulsifying, surface active and micelle forming properties. It is therefore important to lower the T_K of the surfactants for their wider practical use. In previous studies the effect of electrolytes containing a common ion on the T_K and CMC of ionic surfactants has been investigated [103-109]. These studies revealed that CMC decreases in the presence of the added electrolyte. Unfortunately, the added electrolyte that contains a common ion raises the T_K which is unfavorable for their industrial application. Our present study has the major objectives of lowering the CMC and T_K of the surfactant by the addition of electrolytes, investigating surface adsorption and bulk micellar behavior of the surfactant with the help of calculation of thermodynamic parameters and finally carrying out solubilization study of a water insoluble dye with the surfactant in aqueous and in salt solution. In the present study the CMC of the surfactant has been decreased to lower value by adding all the electrolytes which is important from the viewpoint of both fundamental understanding and industrial applications. The present study has revealed that the T_K of the surfactant can be modulated to higher or lower values upon addition of some anions of the Hofmeister series. It is important to note here that the T_K of TTAB increases in presence of Br^- (common ion), SCN^- and I^- and decreases in presence of SO_4^{2-}, Cl^-, NO_3^- and F^-. The explanation of these results has been given on the basis of conventional common ion and salting-in effects along with the concept of the matching water affinities [110,111]. Thus, the presence of electrolytes increases or decreases the T_K, which is an important criterion of surfactants from the solubility viewpoint and industrial applications. The thermodynamic parameters for surface adsorption and micelle formation have also been calculated which extends our knowledge regarding the mechanism surface adsorption and bulk micellization of surfactants in aqueous solution. Moreover, the solubilization study of a water insoluble dye, sudan II with TTAB in pure water and in the presence of NaCl has revealed that MSR value increases in the presence of the salt which indicates higher

solubilization capacity and wider specific applications (solubilization of nonpolar organic compounds) in the presence of the salt.

REFERENCES

1. Mayers, D.; *Surfactant Science and Technology*, 3rd ed., John Wiley & Sons, Interscience, New Jersey, **2006**

2. Rosen, M.J.; *Surfactants and Interfacial Phenomena*, 3rd ed., John Wiley & Sons, Hoboken, **2004**

3. Schramm, L.L.; Stasiuk, E.N.; and Marangoni, D.G.; *Annu. Rep. Prog. Chem. Sect. C* 99, 3, **2003**

4. Holmberg, K.; Jonsson, B.; Kronberg, B.; and Lindman, B.; *Surfactants and Polymers in Aqueous Solution.* John Wiley & Sons, Ltd, **2002**

5. Robb, I.D.; *Specialist Surfactants*, Blackie Academic & Professional, London, **1997**

6. Holmberg, K. Ed.; *Novel Surfactants,* Marcel Dekker, New York, **1998**

7. Myers, D.; *Surfaces, Interfaces, and Colloids: Principles and Applications*, John Wiley & Sons, **1999**

8. Mittal, K.L.; Lindman, B.; *Surfactants in Solution, ed.*, Plenum, New York, vol. 1-3, **1984**

9. Mittal, K.L.; Bothorel, P.; *Surfactants in Solution, ed.*, Plenum, New York, vol. 4–6, **1987**

10. Rosen, M.J.; *Surfactants in Emerging Technologies, ed.*, Dekker, New York, **1987**

11. Lindman, B.; and Wennerstrom, H.; *Top. Curr. Chem.* 87, 1, **1980**

12. Schramm, L.L.; *Emulsions, Fundamentals and Applications in the Petroleum Industry, ed.*, American Chemical Society, Washington DC, **1992**

13. Schramm, L.L.; *Foams, Fundamentals and Applications in the Petroleum Industry, ed.*, American Chemical Society, Washington DC, **1994**

14. Laughlin, R.G.; *J. Soc. Cosmet. Chem.* 32, 371, **1981**

15. Fuhrhop, J-H.; Köning, J.; *In Membranes and Molecular Assemblies: The Synkinetic Approach.Monographs in Supramolecular Chemistry*, The Royal Society of Chemistry: Cambridge, **1994**

16. Patist, A.; Oh, S.G.; Leung, R.; Shah, D.O.; *Coll. Surf. A* 176, 3, **2001**

17. Menger, F.M.; Zana, R.; Lindman, B.; *J. Chem. Ed.* 75, 115, **1998**

18. Tsujii, K.; *In Surface Activity: Principles, Phenomena, and Applications*, Academic Press Ed.: San Diego, London, New York, Tokyo, **1997**

19. Riess, G.; *Prog. Polym. Sci.* 28, 1107, **2003**

20. Frank, H.S.; Evans, M.W.; *J. Phys. Chem.* 13, 507, **1945**

21. Blokzij, W.; Engberts, J.B.F.N.; *Angew. Chem. Int. Ed.* 32, 1545, **1993**

22. Finney, J.L.; Soper, A.K.; *Chem. Soc. Rev.* 23, 1, **1994**

23. Soper, A.K.; Luzar, A.; *J. Phys. Chem.* 100, 1357, **1996**

24. Bowron, D.T.; Filipponi, A.; Lobban, C.; Finney, J.L.; *Chem. Phys. Lett.* 293, 33, **1998**

25. Besseling, N.A.M.; Lyklema, J.; *J. Phys. Chem. B* 101, 7604, **1997**

26. Jorgensen, W.L.; *J. Phys. Chem.* 77, 5757, **1982**

27. Jorgensen, W.L.; Gao, J.; Ravimohan, C.; *J. Phys. Chem.* 83, 3050, **1985**

28. Mancera, R.L.; *J. Chem. Soc. Faraday Trans.* 92, 2547, **1996**

29. Bagno, A.; *J. Chem. Soc., Faraday Trans.* 94, 2501, **1998**

30. Mancera, R.L.; Buckingham, A.D.; *J. Phys. Chem.* 99, 14632, **1995**

31. Engberts, J.B.F.N.; Kevelam; *J. Curr. Opin. Colloid Interface Sci.* 1, 779, **1996**

32. Friberg, S.E.; Liang, Y.C.; *In Microemulsions: Structure and Dynamics*, Boca Raton: CRC Press, **1987**

33. Friberg, S.; Ahmad, *J. Phys. Chem.* 1971, 75, **2001**

34. Shinoda, K.; Nakagawa, T.; Tamamushi, B-I; Isemura, T.; *Colloidal Surfactants, Some Physicochemical Properties*, Academic Press, New York, **1963**

35. Kraift, F.; Wiglow, H.; *Ber.* 28, 2566, **1895**

36. Shinoda, K.; Hutchinson, E.; *J. Phys. Chem.* 66, 577, **1962**

37. Hato, M.; Shinoda, K.; *J. Phys. Chem.* 77, 378, **1973**

38. Cox, K.R.; Benson, H.L.; *The Pseudo-phase Analogy: Application of Vapor-Liquid Equilibria Techniques to Micelle Solution, Fluid Phase Equilibria*, 30, 173 **1986**

39. Aguair, J.; Molina-Bolivar, J.A.; Peula-Garcia, J.M.; Ruiz, C.C.; *J. Colloid & Interface Science* 255, 382, **2002**

40. Islam, M.N.; Kato, T.; *Langmuir* 19, 7201, **2003**

41. Ballerat-Busserolles, K.; Roux-Desgranges, G.; Roux, A.H.; *Langmuir* 13, 1946, **1997**

42. Tadros, T.F.; *Applied Surfactants: Principles and Applications*, Wiley, New York, **2005**

43. Santanu, P.; Pak, K.Y.; *Ind. Eng. Chem. Res.* 45, 3552, **2006**

44. Fanun, M.; *Colloids in Drug Delivery*, CRC Press, **2010**

45. Holmberg, K.; *Handbook of Applied Surface and Colloid* Chemistry, John Wiley & Sons, **2002**

46. Hiemenz, P.C.; Rajagopalan, R.; *Biosurfactants and Biotechnology*, Marcel Dekker, **1997**

47. Saito, S.; *J. Colloid and Interf. Sci.* 24, 227, **1967**

48. Schwuger, M. J.; *Kolloid-Z. Z. Polym*. 240, 872, **1970**

49. Nakagawa, T.; Tori, K.; *Kolloid-Z.* 168, 132, **1960**

50. Roy, J.C.; Islam, M.N.; Aktaruzzaman, G.; *J. Surfact. Deterg.* 17, 231, **2014**

51. Shah, S.S.; Awan, M.A.; Ashraf, M.; Idris, S.A.; *Colloids and Surfaces A* 105, 319, **1995**

52. Elworthy, P.H.; Florence, A.T.; MacFarlane, C.B.; *Solubilization by Surface-Active Agents*. Chapman & Hall, London, 68, **1968**

53. Schramm, L.L.; *Dictionary of Colloid and Interface Science*, John Wiley & Sons, New York, **2001**

54. Mainkar, A.R.; Jolly, C.I.; *Int. J. Cosmet. Sci.* 23, 59, **2001**

55. Umbach, W.; *Prog. Colloid Polym. Sci.* 111, 9, **1998**

56. Schueller, R.; and Romanowski, P.; *Cosmet. Toiletries* 113, 39, **1998**

57. Knoche, M.; *Weed Res.* 34, 221, **1994**

58. Mc Cabe, A.J.; Wilcox, D.T.; Holm, B.A.; Glick, P.L.; *J. Pediatr. Surg.* 35, 1687, **2000**

59. Hamm, H.; Kroegel, C.; Hohlfeld, J.; *J. Respir. Med.* 90, 251, **1996**

60. Bibette, J.; Calderon, F.L.; Poulin, P.; *Rep. Prog. Phys.* 62, 969, **1999**

61. Hofmeister, F.; *Arch. Exp. Pathol. Pharmacol.* 24, 247, **1888**

62. Kunz, W.; Henle, J.; Ninham, B.W.; *Curr. Opin. Colloid Interface Sci.* 9, 19, **2004**

63. Broering, J.M.; Bommarius, A.S.; *J. Phys. Chem. B* 109, 20612, **2005**

64. Xiong, K.; Asciutto, E.K.; Madura, J.D.; Asher, S.A.; *Biochemistry* 48, 10818, **2009**

65. Pinna, M.C.; Bauduin, P.; Touraud, D.; Monduzzi, M.; Ninham, B.W.; Kunz, W.; *J. Phys. Chem. B* 109, 16511, **2005**

66. Pinna, M.C.; Salis, A.; Monduzzi, M.; Ninham, B.W.; *J. Phys. Chem. B* 109, 5406, **2005**

67. Bauduin, P.; Nohmie, F.; Touraud, D.; Neueder, R.; Kunz, W.; Ninham, B.W.; *J. Mol. Liq.* 123, 14, **2006**

68. Vrbka, L.; Jungwirth, P.; Bauduin, P.; Touraud, D.; Kunz, W.; *J. Phys. Chem. B* 110, 7036, **2006**

69. Perez-Jimenez, R.; Godoy-Ruiz, R.; Ibarra-Molero, B.; Sanchez-Ruiz, J.M.; *Biophys. J.* 86, 2414, **2004**

70. Curtis, R.A.; Lue, L.; *Chem. Eng. Sci.* 61, 907, **2006**

71. Collins, K.D.; *Methods* 34, 300, **2004**

72. Lo Nostro, P.; Ninham, B.W.; Milani, S.; Fratoni, L.; Baglioni, P.; *Biopolymers* 81, 136, **2006**

73. Lo Nostro, P.; Ninham, B.W.; Lo Nostro, A.; Pesavento, G.; Fratoni, L.; Baglioni, P.; *Phys. Biol.* 2, 1, **2005**

74. Ninham, B.W.; Yaminsky, V.; *Langmuir* 13, 2097, **1997**

75. Bostrom, M.; Kunz, W.; Ninham, B.W.; *Langmuir* 21, 2619, **2005**

76. Srinivasan, V.; Blankschtein, D.; *Langmuir* 19, 9932, **2003**

77. Srinivasan, V.; Blankschtein, D.; *Langmuir* 19, 9946, **2003**

78. Bostrom, M.; Williams, D.R.M.; Ninham, B.W.; *Langmuir* 18, 6010, **2002**

79. Hennig, A.; Fischer, L.; Guichard, G.; Matile, S.; *J. Am. Chem. Soc.* 131, 16889, **2009**

80. Sovago, M.; Wurpel, G.W.H.; Smits, M.; Muller, M.; Bonn, M.; *J. Am. Chem. Soc.* 129, 11079, **2007**

81. Aroti, A.; Leontidis, E.; Maltseva, E.; Brezesinski, G.; *J. Phys. Chem. B* 108, 15238, **2004**

82. Zhang, Y.J.; Furyk, S.; Bergbreiter, D.E.; Cremer, P.S.; *J. Am. Chem. Soc.* 127, 14505, **2005**

83. Zhang, Y.J.; Furyk, S.; Sagle, L.B.; Cho, Y.; Bergbreiter, D.E.; Cremer, P.S.; *J. Phys. Chem. C* 111, 8916, **2007**

84. Collins, K.D.; Washabaugh, M.W.; *Q. Rev. Biophys.* 18, 323, **1985**

85. Omta, A.W.; Kropman, M.F.; Woutersen, S.; Bakker, H.J.; *Science* 301, 347, **2003**

86. Batchelor, J.D.; Olteanu, A.; Tripathy, A.; Pielak, G.J.; *J. Am. Chem. Soc.* 126, 1958, **2004**

87. Gurau, M.C.; Lim, S.M.; Castellana, E.T.; Albertorio, F.; Kataoka, S.; Cremer, P.S.; *J. Am. Chem. Soc.* 126, 10522, **2004**

88. Chen, X.; Yang, T.L.; Kataoka, S.; Cremer, P.S.; *J. Am. Chem. Soc.* 129, 12272, **2007**

89. Smith, J.D.; Saykally, R.J.; Geissler, P.L.; *J. Am. Chem. Soc.* 129, 13847, **2007**

90. Bostrom, M.; Williams, D.R.M.; Ninham, B.W.; *Phys. Rev. Lett.* 87, 168103, **2001**

91. Jungwirth, P.; Tobias, D.J.; *J. Phys. Chem. B* 105, 10468, **2001**

92. Jungwirth, P.; Tobias, D.J.; *J. Phys. Chem. B* 106, 6361, **2002**

93. Zhang, Y.J.; Cremer, P.S.; *Curr. Opin. Chem. Biol.* 10, 658, **2006**

94. Jungwirth, P.; Winter, B.; *Annu. Rev. Phys. Chem.* 59, 343, **2008**

95. Islam, M.N.; Sharker, K.K.; Sarker, K.C.; *J. Surfact. Deterg.* 18, 651, **2015**

96. Francis, M.F.; Piredda, M.; Winnik, F.M.; *J. Controlled Release* 93, 59, **2003**

97. Liu, C.; Desai, K.G.H.; Liu, C.; *J. Chem. Eng. Data* 49, 1847, **2004**

98. Paria, S.; Yuet, P.K.; *Ind. Eng. Chem. Res.* 45, 3552, **2006**

99. Lee, J.; Moroi, Y.; *Langmuir* 20, 6116, **2004**

100. Islam, M.N.; Sarker, K.C.; Sharker, K.K.; *J. Surfact. Deterg.* 18, 9, **2015**

101. Tsuji, K.; Mino, J.; *J. Phys. Chem.* 82, 1610, **1978**

102. Chu, Z.; Feng, Y.J.; *Langmuir* 28, 1175, **2012**

103. Shinoda, K.; Yamaguchi, N.; Carlsson, A.; *J. Phys. Chem.* 93, 7216, **1989**

104. Carolina, V-G; Bales, B.L.; *J. Phys. Chem. B* 107, 5398, **2003**

105. Michele, A.D.; Brinchi, L.; Profio, P.D.; Germani, R.; Sawelli, G.; Onori,G.; *J. Colloid Interf. Sci.* 358, 160, **2011**

106. Mata, J.; Varade, D.; Bahadur, P.; *Thermochim Acta* 428, 147, **2005**

107. Bojan, S.; Marija, B-R; *J. Colloid Interf. Sci.* 338, 216, **2009**

108. Nakahara, H.; Shibata, O.; Moroi, Y.; *J. Phys. Chem. B* 115, 9077, **2011**

109. Heckmann, K.; Schwarz, R.; Strnad, J.; *J. Colloid Interf. Sci.* 120, 114, **1987**

110. Collins, K.D.; *Biophys. Chem.* 167, 43, **2012**

111. Collins, K.D.; Neilson, G.W.; Enderby, J.E.; *Biophys. Chem.* 128, 95, **2007**

CHAPTER TWO

EXPERIMENTALS

2.1 CHEMICALS

2.1.1 Surfactant

Tetradecyltrimethylammonium bromide (TTAB)

Molecular formula: $CH_3(CH_2)_{13}N(Br)(CH_3)_3$

Structure:

The cationic surfactant tetradecyltrimethylammonium bromide (TTAB) was supplied by Sigma-Aldrich with a purity of >99% and was used as received.

2.1.2 Salts

1. Sodium chloride (NaCl)

2. Sodium bromide (NaBr)

3. Sodium iodide (NaI)

4. Sodium fluoride (NaF)

5. Sodium thiocyanate (NaSCN)

6. Sodium nitrate (NaNO$_3$)

7. Sodium sulfate (Na$_2$SO$_4$)

The salts were obtained from MERCK, BDH and Sigma-Aldrich with a purity of >99% and were used as received.

2.1.3 Dye

1-(2,4-dimethylphenyl) azonapthalen-2-ol, Common name: Sudan II

Molecular formula: $C_{18}H_{16}N_2O$

Structure:
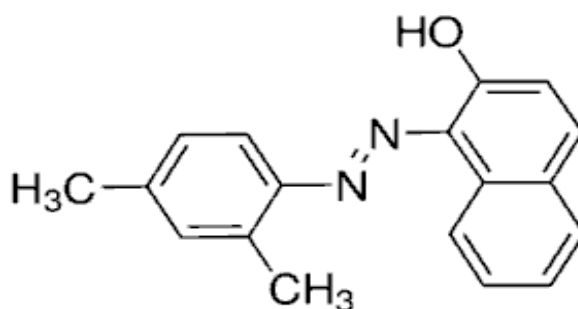
The water insoluble dye sudan II was obtained from BDH.

2.2 MEASUREMENTS

2.2.1 Krafft temperature

In order to determine T_K, 0.0075 M solution of TTAB in pure water and in the presence of different electrolytes of different concentrations was prepared. The solution was then placed in a refrigerator at about 2^oC until hydrated crystals of surfactant were formed. The system was then taken out of the refrigerator and placed in a circulating water bath (HAAKE F3) to control the temperature of the system. The conductance of the system was measured by a EUTECH CON 510 conductivity meter. As the temperature of the system was gradually increased, after taking the κ reading at a specific temperature the system was then stirred by a stirrer so that the temperature increases homogeneously in the system. The κ reading at each temperature was taken when steady value was obtained. When κ is plotted against temperature, the T_K is determined from an abrupt change of κ at a narrow temperature range. T_K was also measured visually in some cases as it is the temperature at which hydrated crystals of surfactant are completely dissolved and a clear solution is obtained [1]

2.2.2 Critical micelle concentration

Conductometric method: To determine the CMC by conductometric method a EUTECH CON 510 conductivity meter was used. A single CMC measurement experiment was started with a dilute solution and the solution was successively concentrated by previously prepared stock solution injected by a 1 mL graduated pipette into a 100 mL beaker. The solution was stirred with a glass rod after each injection to make the solution homogeneous. The CMC was determined from the sharp break in the κ versus concentration plot. The temperature was controlled by a HAAKE F3 refrigerated bath circular with a temperature precision of ±0.1°C. In order to determine the CMC in presence salts, solutions of surfactant were prepared in various salts solutions of desired concentrations [2].

Surface tensiometric method: In order to determine the CMC in surface tensiometric method, the surface tensions of solutions of surfactant in pure water and in presence of various electrolytes were measured by a surface tensiometer (Kruss K9) equipped with a platinum plate. The platinum plate was thoroughly washed by red hot of Bunsen burner. Before starting experiment at a specific temperature, the surface tension of the double distilled water was confirmed to be in the range of ±0.2 mN/m. The previously prepared stock solution is then successively injected to this vessel by a 1 mL graduated pipette and the surface tension is carefully measured. The deviation in taking a reading was ±0.2 mN/m. The reading of surface tension was taken 10 minutes after the injection in order to ensure the establishment of equilibrium. The CMC was then determined from the breakpoint in the γ versus $\log_{10}C$ plot. Details of the experimental procedure are to be found elsewhere [3].

2.3 SOLUBILIZATION STUDY

The solubilization study of sudan II with TTAB was carried out in pure water and in presence of NaCl under the condition of maximum solubilization at room temperature. There was no problem had to be faced to conduct solubilization study at this temperature because this temperature is far above the Krafft temperature of TTAB. 50 mL reagent bottles were used for the study. These reagent bottles were filled with 25 mL of surfactant solutions of different concentrations (some below the

CMC and some above the CMC) and a fixed as well as excess amount of dye so that solubilization equilibrium could be achieved. In order to attain solubilization equilibrium, the reagent bottles were continuously shaken by using a shaker (Stuart Orbital Shaker, SSL1) with a rotation speed of 250 rpm for about 24 hours. The solutions were then filtered to separate the amount of dye that was not solubilized by using Whatman 41 Ashless Quantitative Filter Paper with a pore size of 2.5 μm. The filtrate of each solution was taken in a quartz cell of path length 1 cm and the absorbance was measured by a UV-visible spectrophotometer (Jenway Spectrophotometer 7315). The concentration of sudan II that is solubilized by surfactant micelles was calculated from a calibration curve obtained from the absorption spectra of known concentrations of sudan II in TTAB against a blank. The strong absorbance was found at λ_{max}= 496 nm which gave a satisfactory Beer's law plot.

REFERENCES

1. Islam, M.N.; Sarker, K.C.; Sharker, K.K.; *J. Surfact. Deterg.* 18, 9, **2015**
2. Islam, M.N.; Sharker, K.K.; Sarker, K.C.; *J. Surfact. Deterg.* 18, 651, **2015**
3. Roy, J.C.; Islam, M.N.; Aktaruzzaman, G.; *J. Surfact. Deterg.* 17, 231, **2014**

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 EFFECT OF ADDED ELECTROLYTES ON THE KRAFFT TEMPERATURE OF TTAB

Figure 3.1 shows the specific conductance (κ) versus temperature curve of TTAB in pure water and in presence of different electrolytes of ionic strength 0.0025. At low temperatures, the solubility of TTAB is very limited as it forms solid hydrates indicated by the low specific conductance (κ) of the solution. Initially the κ values increase very slowly with increasing temperature and then increase sharply over a narrow temperature range showing a clear break point in the κ-T plots. This break point is an indication of the sharp increase in the solubility of surfactant system and is called the Krafft temperature (T_K) of the surfactant. The Krafft temperature is known as the temperature at and above which a rapid increase in the solubility of an ionic surfactant in water begins to appear due to micelle formation [1]. On the basis of the pseudo-phase separation model of the micellar solution, the T_K is the melting point of a hydrated solid surfactant [2-5]. The T_K value of TTAB in pure water is found to be 11.6ºC. This value is found to be in good agreement with the literature value [6]. In the present study the effect of some added counter ions on the T_K of TTAB in aqueous system has been investigated. It was observed that the solubility and thereby, the T_K of TTAB increases or decreases in presence of added counter ions depending on the size and charge density of the ions. It is clear from the Figure 3.1 and 3.2 that the T_K of TTAB increases in presence of ions of low charge density as: Br^-, SCN^- and I^- while decreases in presence of ions of high charge density as: F^-, SO_4^{2-}, Cl^- and NO_3^- at ionic strength of 0.0025 of the ions and this increase or decrease of T_K shows a gradual trend with increasing the ionic strength of the ions. An anomalous behavior is observed in case of SCN^- ion at ionic strength of 0.0010. At this ionic strength the T_K is lower than that of pure TTAB and the reason behind this will be discussed later. The T_K in presence of SO_4^{2-} and Cl^- at ionic strength beyond 0.005 and in presence of NO_3^- at ionic strength beyond 0.0025 could not be determined because of no solid hydrates formation. The T_K in the presence of I^- at ionic strength 0.0075 was determined visually but not conductometrically because of the high probability of vaporization. A slight decrease in solubility with a consequent slight increase in T_K of TTAB in aqueous system in presence of Br^- can be attributed to the common ion effect. This observation is in line with the previous studies of Islam M.N. et al. for gradual increase of T_K of benzyldimethylhexadecylammonium chloride (C16Cl) [2]

and cetylpyridinium bromide (CPB) [1] in the presence of their respective common ions in aqueous systems.
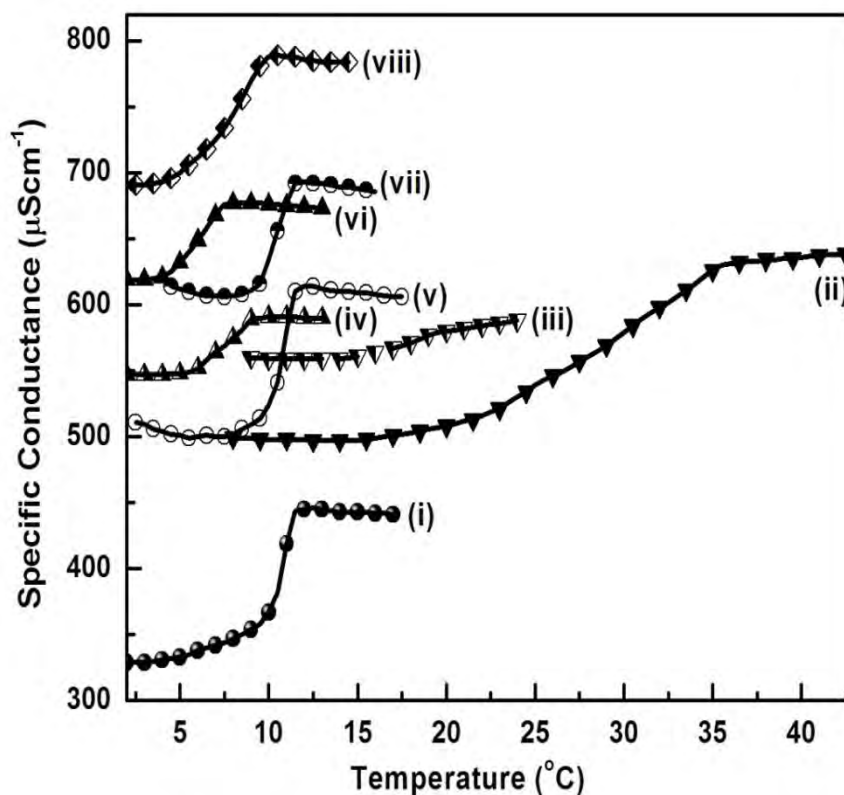
Figure 3.1: Specific conductance vs. temperature plots of TTAB in pure water and in presence of different electrolytes of ionic strength 0.0025. (i) Pure TTAB, (ii) NaI, (iii) NaSCN, (iv) Na$_2$SO$_4$, (v) NaBr, (vi) NaNO$_3$, (vii) NaF and (viii) NaCl

The interaction between the ions and the surfactant molecules is influenced by the interfacial water structure. It was revealed by vibrational sum frequency experiments that water molecules at the interface are oriented in such a way that the hydrogen atoms are directed toward the bulk with the oxygen atom pointed toward the gas phase [7,8]. The final result of this orientation of water molecules is the formation of a double layer with a negative outermost surface directed upward to the gaseous phase while the positively charged surface is directed downward to the solvent side. Therefore, it is reasonable to expect a preferential accumulation of anions near the interface with the positive portion of the double layer. However, the extent of accumulation of the anions at the interface is influenced by their relative tendency of hydration in the bulk.
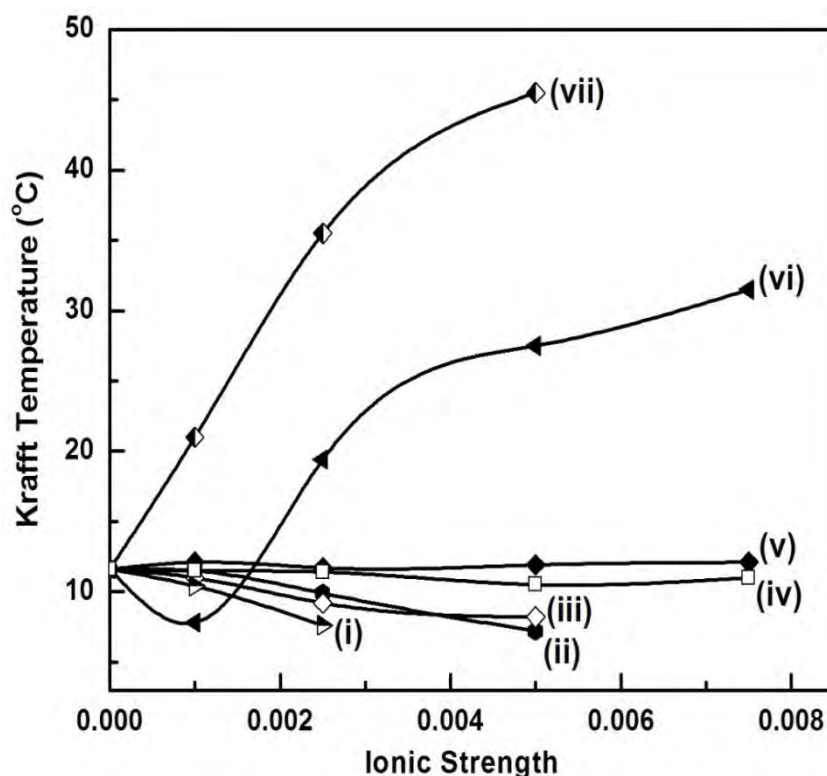
Figure 3.2: Effect of ionic strength of electrolytes on the Krafft temperature of TTAB. (i) NaNO$_3$, (ii) NaCl, (iii) Na$_2$SO$_4$, (iv) NaF, (v) NaBr, (vi) NaSCN and (vii) NaI

Islam M.N. et al. [9] reported that the increase in surface tension of SO$_4^{2-}$, F$^-$, Cl$^-$, Br$^-$, NO$_3^-$, SCN$^-$ and I$^-$ at 25°C are found to be 3.1, 2.0, 1.6, 1.3, 1.0, 0.4 and 0.8 (mN/m)/(mol/L) respectively. Thus, it appears from the data that SO$_4^{2-}$ has the greatest ability to increase the surface tension relative to pure water, and the trend decreases according to the Hofmeister series [10]. This means that the more kosmotropic ions preferentially remain in the bulk because of their strong tendency for hydration showing negative adsorption behavior according to the Gibbs adsorption equation [7]. Weakly hydrated SCN$^-$ and I$^-$ are known to be chaotropes having a preferential tendency to accumulate at the air-water and low solvated hydrocarbon-water interface. This type of behavior of accumulation at the air-water interface is termed as positive adsorption behavior according to the Gibbs adsorption equation. It was shown by Levin and Santos that the kosmotropic ions remain hydrated near the interface and are repelled from it, while the chaotropic ions lose their hydration sheath and tend to accumulate at the air-water as well as low solvated hydrophobic interface

[11]. Water molecules interact with individual ions in the way which is dependent on the charge density and extent of hydration of the ions. The behavior of the ions in the high dielectric regime of water is controlled by the electrochemical processes mentioned above which favor weakly hydrated anions to adsorb favorably at the air-water and low solvated hydrocarbon-water interface [12]. It was reported by Cremer and coworkers that the accumulation of the weakly hydrated chaotropes can interfere with hydrophobic hydration by increasing the surface tension of the hydrocarbon-water interface and exhibit salting out behavior of macromolecules [13]. Therefore, it is reasonable to expect that these ions will be preferentially accumulated at the surface of the hydrophobic chain of the surfactant. This directly disturbs the hydrophobic hydration of the surfactant resulting in salting out behavior with a consequent increase in the T_K.

The law of matching water affinities which is an important proposal of Collins' can be applied to explain the extent of interaction between the ions in aqueous solution [12,14]. This interaction is associated with the competition between the charge density dependent ion-water interactions and hydrogen bond dominated water-water interactions. The basic theme of this concept includes chaotropes can form contact ion pairs with other chaotropes as much as kosmotropes with other kosmotropes. As chaotropes and kosmotropes have large difference in their water affinities, chaotropes do not come into close contact with kosmotropes. The weakly hydrated chaotropes cannot break through the hydration shell of the strongly hydrated kosmotropes and therefore such ions form a highly soluble solvent separated pairs [14]. From the view point of molecular dynamic simulations, Heyda et al. established that the pairing of tetraalkylammonium (TAA) ions with heavier halides is increasingly preferred over lighter halides when the chain length of TAA becomes gradually longer [15]. As the chain length of TAA increases, the sterical constraints to the spatial distribution of water molecules also increase resulting in a weak hydration of the ion. As TTAB bears a 14-carbon alkyl chain along with three methyl groups, the cationic part of the surfactant can be expected to behave like a chaotrope. Moreover, it was previously reported that heavy anions produce a weak electric field which is not adequate to bind the adjacent water molecules strongly and are preferentially adsorbed near the interface. Besides, the organization of the hydrogen bonding network in bulk water molecules is much better in absence of these ions and as a consequence they tend to

interact with the counterions of similar water affinities. Therefore, it can be expected that weakly hydrated chaotropes SCN^- and I^- will readily form contact ion pairs with the weakly hydrated tetradecyltrimethylammonium ion. Beek and Mandel reported that polarizability of water molecules is obstructed in presence of the electrolytes and results in a decrease in the dielectric constant of water [16]. This favors the formation of contact ion pairs when the system contains ions of matching water affinities. Again, the electrostatic repulsion between the surfactant ions is decreased by the chaotropic anions as they effectively screen the head group charge promoting salting-out behavior with a consequent increase in T_K. Such a salting-out behavior of macromolecules in the presence of the strong chaotropes was previously observed [17]. An irregular behavior of T_K is observed in presence of 0.001 M SCN^- solution. At this concentration of SCN^-, T_K is lower than that of pure TTAB. As previously mentioned, the increase in surface tension for SCN^- is 0.4 (mN/m)/(mol/L) and this value is lowest in compared to the other ions [9]. So, SCN^- has the greatest ability to adsorb at the interface. When SCN^- is adsorbed at the interface, the hydrogen bonding network of water molecules at the interface is broken. As a result, the number of monomeric water molecules increase and hydration of the surfactant is significantly enhanced. This gives the TTAB molecules an increased solubility with a consequent decrease in the T_K. With an increased concentration of SCN^- no further adsorption occurs because the interface is fully occupied. Under this condition, formation of contact ion pairs between SCN^- and TTAB occurs in the bulk resulting in a decrease in solubility and thereby an increase in T_K. Ions of smaller size have higher charge density and have the capability to bind the water molecules more tightly around the hydration sphere. Therefore, less chaotropic Cl^- and NO_3^- should exhibit higher tendency for hydration than more chaotropic SCN^- and I^-. It was previously reported that when an ion is more strongly hydrated than its counterpart, their pairing is not thermodynamically favorable because the energy required to lose the hydrated water shell of the more strongly hydrated ion is higher than the energy gained by forming contact ion pair with the weakly hydrated counterpart. Therefore, these ions tend to stay away from one another and being separated by the solvent molecules. Thus, in the presence of these ions the surfactant molecules disperse and consequently the T_K of the surfactant decreases. It has been shown from neutron and X-ray diffraction experiments that considerably less hydrogen bonding exists in the presence of

chaotropes than in pure water in the absence of an electrolyte [18]. Furthermore, nuclear magnetic resonance studies demonstrate that the water molecules adjacent to a chaotrope tumble more rapidly than in the bulk of the solution as expected for a water molecule that is not held by its neighbors through hydrogen bonding [19]. Therefore, the concentration of free water molecules increases in the presence of chaotropic NO_3^- and this promotes hydration of the surfactant with a consequent decrease in T_K. Moreover, according to the principle of salting-in effect, the solubility of a sparingly soluble salt increases in the presence of an added salt having no common ions when the activity coefficient is less than 1 [20]. The activity coefficient decreases gradually with increasing the ionic strength of added electrolytes. In order for the thermodynamic solubility product to be constant the solubility of the sparingly soluble salt would increase. In the present work the ionic strength of all the salt solutions has kept within 0.0075 to investigate the salt effect on the T_K of TTAB, where the activity coefficients of the salts in the solution remain below unity. Such a salting-in effect with a consequent decrease in the T_K in presence of added NO_3^- of CPB [1] and C16Cl [2] was observed previously.

Our present study reveals that kosmotropic SO_4^{2-} and F^- (to some extent) decrease the T_K of TTAB. The effect of SO_4^{2-} and F^- on the T_K of TTAB can be explained in a different way as these ions interact dissimilarly with the surfactant compared to the rest of the ions. It is mentioned before that the molar increase in surface tension is higher in presence of SO_4^{2-} and F^- than that of pure water and in presence of other ions. Relatively higher molar increases in surface tension gives an indication that the concentration of these ions in the bulk is much higher than at the air-water interface because of their tendency for extensive hydration. An explanation of the increase in surface tension of aqueous salt solutions can be brought from the Gibbs adsorption equation in terms of negative adsorption [7]. Kosmotropic SO_4^{2-} and F^- having high charge density remain strongly hydrated in the bulk. Therefore, it is expected that these ions do not show any tendency to lose the hydration shell to form a contact ion pair with the weakly hydrated cationic part of the surfactant. Thus, these ions form solvent-separated ion pairs with high solubility. The presence of kosmotropic SO_4^{2-} and F^- ions favors dispersion of the surfactant in the aqueous solution leading to an increase in solubility with a decrease in the T_K. In the present study it has been found

that NO_3^- has the greatest ability to lower the T_K and the trend follows the order: $NO_3^- > SO_4^{2-} > Cl^- > F^- > Br^- > SCN^- > I^-$. Thus it appears that even though SO_4^{2-} is a strong kosmotrope, its role in term of lowering the T_K is almost as pronounced as chaotropic NO_3^-. Chen et al. [21] reported that when the protein surface is positively charged, SO_4^{2-} shifts from its usual position in the Hofmeister series and behaves more like a chaotropic ion exhibiting salting-in effect. This phenomenon was explained by them on the basis of electrostatic interactions. As the nitrogen present in TTAB is positively charged, this phenomenon can be hold in the present case. Such a shift of SO_4^- from its usual position in the Hofmeister series in terms of lowering the T_K was also observed previously [1,2]. When the added salt contains an ion in common with that of the surfactant as in the present case the common ion effect dominates over the salting-in effect. According to the principle of common ion effect, when a sparingly soluble salt is in equilibrium with its ions, addition of an electrolyte having an ion in common decreases the solubility of the sparingly soluble salt so that the constancy of the solubility product of the ions involved in equilibrium could be maintained [5,20]. Therefore, in order to maintain the constancy of the solubility product, the solubility of TTAB decreases in presence of Br^-, showing a slight increase in the T_K of TTAB.

3.2 SURFACE ADSORPTION AND BULK MICELLIZATION OF TTAB IN PURE WATER AND IN PRESENCE OF ADDED ELECTROLYTES

The micellization of ionic surfactants is the result of aggregation of surfactant monomers and this aggregation is controlled by the favorable interaction between the hydrophobic alkyl chains and opposing repulsive interaction between the charged headgroups along with the extent of screening of the micelle surface charge by associated counterions [22-24]. The aggregation of surfactant monomers in the bulk into micelles begins at a definite surfactant concentration when all the surface and interface are occupied by the surfactant monomers. This definite value of concentration of surfactant is called critical micelle concentration (CMC). In our present work the CMC of TTAB is measured in pure water and in presence of electrolytes by conductometric and surface tensiometric methods above the T_K of the surfactant. The studied temperature range was 15-35°C for TTAB in pure water and in presence of NaCl of ionic strength 0.0025. The CMC is also measured at 25°C for other electrolytes of ionic strength 0.0025. Below the T_K we could not measure the CMC because at this temperature precipitation of hydrated crystals occurs and above 35°C the vaporization of water occurs which changes the solution concentration and also the practical use of surfactants solution is rather limited above this temperature. The T_K can increase when the salt to surfactant concentration ratio is too high [25]. At 0.0025 ionic strength of the salt, the T_K of the TTAB remains below 25°C in the presence of the most electrolytes (studied in this work) except SCN^- and I^- ions. Therefore, we could not measure the CMC of surfactant in the presence of SCN^- and I^- ions. Figure 3.3(a-f) show the specific conductance (κ) versus surfactant concentration plots at 25°C for TTAB in pure water and in presence of SO_4^{2-}, NO_3^-, Br^-, Cl^- and F^- respectively.
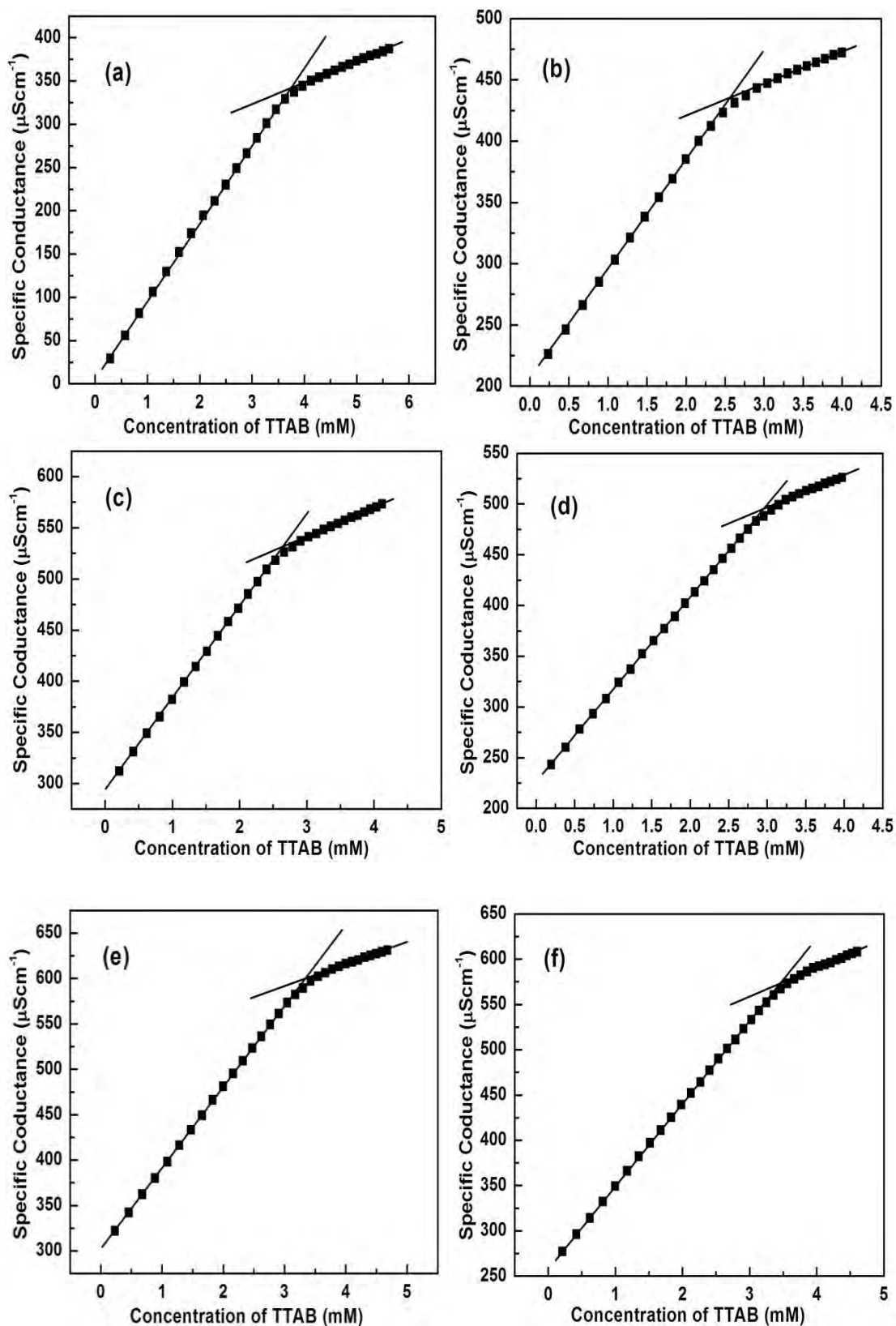
Figure 3.3: Specific conductance vs. concentration plots of TTAB in pure water and in presence of different electrolytes of ionic strength 0.0025 at 25°C. (a) Pure TTAB, (b) Na₂SO₄, (c) NaNO₃, (d) NaBr, (e) NaCl and (f) NaF

It is observed from each figure that the κ increases progressively with increasing the concentration of the surfactant. This is due to the increase in the number of surfactant monomers with increase in the surfactant concentration. The break point in the κ versus surfactant concentration plot is an indication of the formation of micelles from surfactant monomers with part of the charge of the micelle neutralized by the associated counter-ions. The CMC is determined from the intersection point of two slopes. Surface tensiometric method has also been applied to determine the CMC values of TTAB in pure water and in presence of different salts. Figure 3.4(a-f) show the surface tension (γ) versus logarithm of concentration ($\log_{10}C$) plots at 25°C for TTAB in pure water and in presence of SO_4^{2-}, NO_3^-, Br^-, Cl^- and F^- respectively. The surface tension (γ) progressively decreases with increasing the surfactant concentration which is a consequence of spontaneous adsorption of surfactant molecules from the bulk of the aqueous solution to the air-water interface. From each figure, it can be seen that γ decreases up to the CMC beyond which almost constant values are obtained because of the saturation of the solution surface by the adsorbed surfactant monomers. When full saturation of the air-water interface occurs due to adsorption of surfactant monomers, further increase in surfactant concentration contributes only to form micelles in the bulk. The intersection point of γ versus $\log_{10}C$ plot indicates the CMC. Although the CMC determined by different methods differs to some extent but a good reproducibility of data is obtained from an individual method [26]. The CMC obtained from the surface tensiometric method is slightly lower than that of the conductometric method and it is depicted in Table 3.1, and is in good agreement with the literature value [26-28]. Table 3.1 shows the CMC of TTAB in pure water and in presence of added salts obtained by the two methods. It can be seen from the table that the CMC decreases considerably in presence of the added electrolytes, favoring aggregation of the surfactant molecules in the bulk of the aqueous solution. The efficiency of lowering the CMC is dependent on the nature of the added counterion.
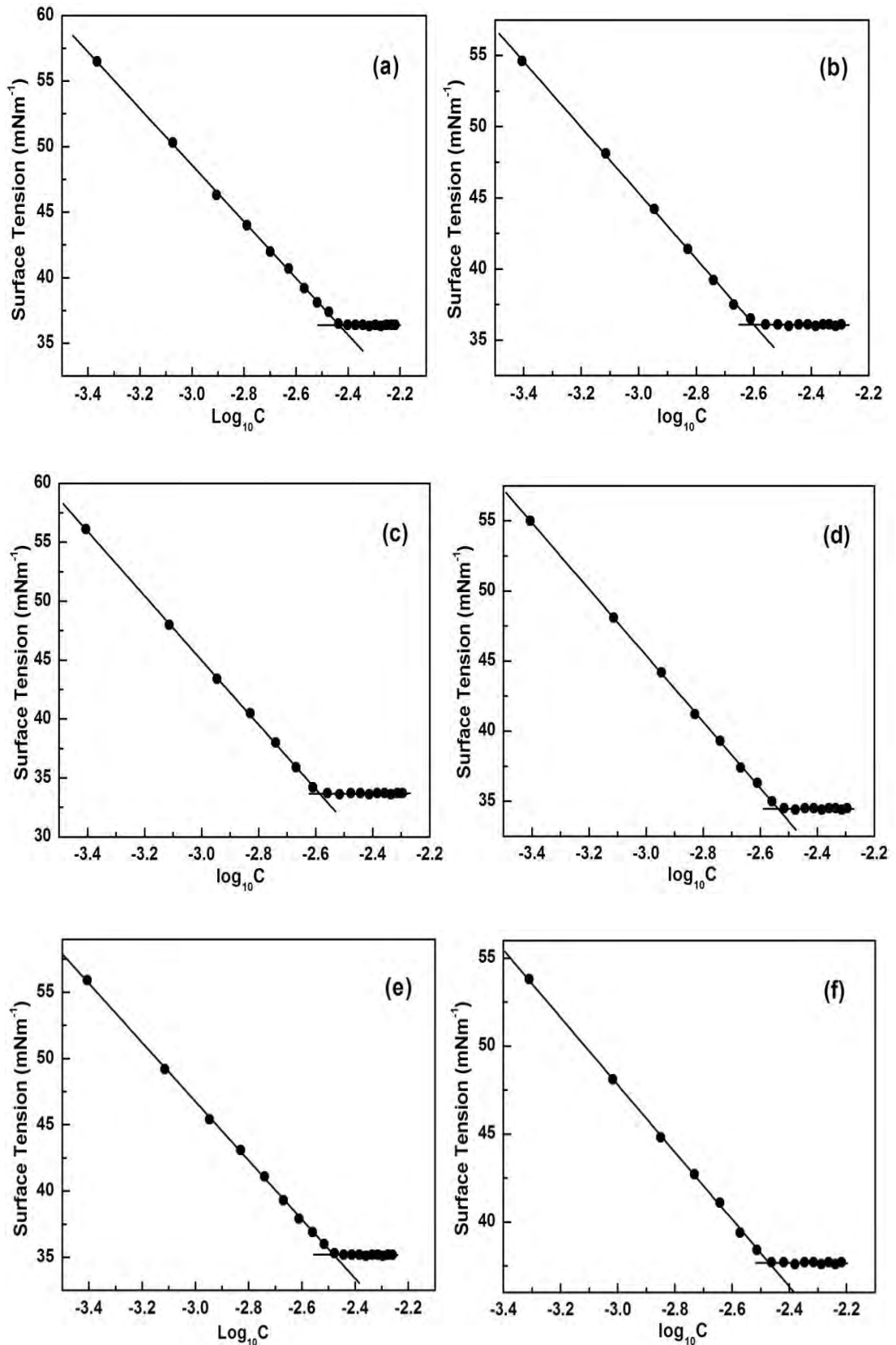
Figure 3.4: Surface tension vs. Log$_{10}$C plots of TTAB in pure water and in presence of different electrolytes of ionic strength 0.0025 at 25°C. (a) Pure TTAB, (b) Na$_2$SO$_4$, (c) NaNO$_3$, (d) NaBr, (e) NaCl and (f) NaF

It is observed in the present study that SO_4^{2-} is most efficient in lowering the CMC, and the tendency of lowering the CMC follows the trend: $SO_4^{2-} > NO_3^- > Br^- > Cl^- > F^-$, with F^- being less efficient in lowering the CMC. The counterions adsorb at micelle surface and screen the charge of the surfactant headgroups. The screening of the micelle surface charge lessens the electrostatic repulsion between the charged headgroups. This results in the closer packing of the surfactant headgroups, which facilitates micellar aggregation at a much lower surfactant concentration. The lowering of CMC in presence of added electrolytes (containing a common ion to that of the surfactant) was also observed previously [24,27-29]. It has been found in the previous reports that when a surfactant solution contains more than one counter ion then a competitive adsorption of ions occurs. In such a situation, multivalent ion exhibit greater tendency for adsorption onto the micelle surface compared to the monovalent one [30,31]. Therefore, doubly charged SO_4^{2-} should exhibit greater interaction with the TTAB headgroup compared to the rest of the monovalent ions. The effect of screening the net positive charge of the micelle surface is double for SO_4^{2-} compared to the monovalent ions and it promotes closer packing of the charged headgroups and therefore micellar aggregation at comparatively lower surfactant concentration. As nitrogen based cations behave like chaotrope, therefore tetradecyltrimethylammonium ion should interact with large anions. When large chaotropic anions adsorbed at micelle surface, they make contribution to screen the head group charge as well as close packing of molecules with a subsequent lowering of CMC. It has been previously proposed that kosmotropes and chaotropes have different interactions with their counterparts [32]. The interaction of weakly hydrated chaotropes with oppositely charged headgroups is strong and close packing of headgroups in the micelle is the result of this strong interaction. On the contrary, strongly hydrated kosmotropes have no tendency to lose their hydrated shell. As a kosmotrope F^- is strongly hydrated, it cannot approach at the close proximity of micelle surface. Thus, NO_3^- and Br^- are more effective in lowering the CMC compared to Cl^- and F^-.

Table 3.1: The CMC of TTAB in pure water and in different electrolyte solutions of ionic strength 0.0025 at 25°C (298K)

System	CMC in surface tensiometric measurement (mM)	CMC in conductometric measurement (mM)
Pure TTAB	3.69	3.75
NaCl	3.31	3.34
Na$_2$SO$_4$	2.52	2.56
NaBr	2.90	2.95
NaF	3.38	3.45
NaNO$_3$	2.59	2.64

Figure 3.5 shows the variation of CMC of TTAB with temperature in pure water and in presence of NaCl. It is evident from the figure that in both cases CMC increases with increasing temperature over the studied temperature range. The CMC value of a surfactant at a definite temperature is governed by the balance between two interactions as: the van der Waals interaction between the hydrophobic alkyl groups that has a tendency to stabilize the micelle and the opposing repulsive interaction between the charged headgroups that has a tendency to break up the micelles. The effect of temperature on the CMC of surfactants is usually analyzed in terms of two opposing factors. First, as the temperature increases the degree of hydration of the hydrophilic group decreases, which favors micellization and the second factor is an increase in temperature also causes the disruption of water structure surrounding the hydrophobic group and this is unfavorable to micellization [28,33]. In the present study we have found that the CMC values of TTAB in pure water and in presence of NaCl increase with increasing temperature indicating that the second effect predominates over the first one within the studied temperature range.
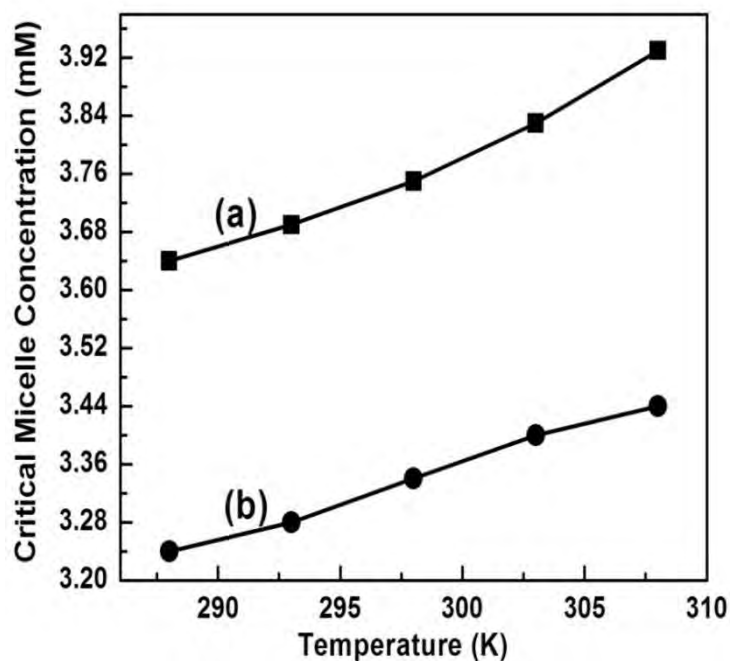
Figure 3.5: Dependence of CMC on temperature of TTAB in (a) pure water and (b) in presence of 0.0025 M NaCl solution (CMC values for this plot is taken from conductometric measurement)

Table 3.2: The CMC of TTAB in pure water and in 0.0025 M NaCl solution at different temperatures

Temp. (K)	CMC (mM) in pure water		CMC (mM) in 0.0025 M NaCl solution	
	Surface tensiometric measurement	Conductometric measurement	Surface tensiometric measurement	Conductometric measurement
288	3.61	3.64	3.21	3.24
293	3.66	3.69	3.24	3.28
298	3.69	3.75	3.31	3.34
303	3.74	3.83	3.34	3.40
308	3.80	3.93	3.38	3.44

The minimum concentration of a surfactant required to produce maximum reduction in surface tension at a particular temperature is important from the view point of the effectiveness of a surfactant. It is well-known that at a definite temperature when the concentration of the surfactant solution is $\geq$ the CMC of the surfactant, then maximum reduction in surface tension (minimum γ value) can be exhibited by the surfactant solution. The significance of the Krafft temperature (T_K) in this regard can be rationalized with the help of γ vs. temperature plot shown in Figure 3.6. For this purpose we prepared a 3.64×10^{-3} M solution of TTAB and cooled to about 1°C, then raised the temperature gradually and measured the equilibrium surface tension of the solution. It is evident from this observation that maximum reduction in surface tension occurs when the temperature of the system reaches around 11°C and below this temperature the γ value is much lower than the minimum attainable value.
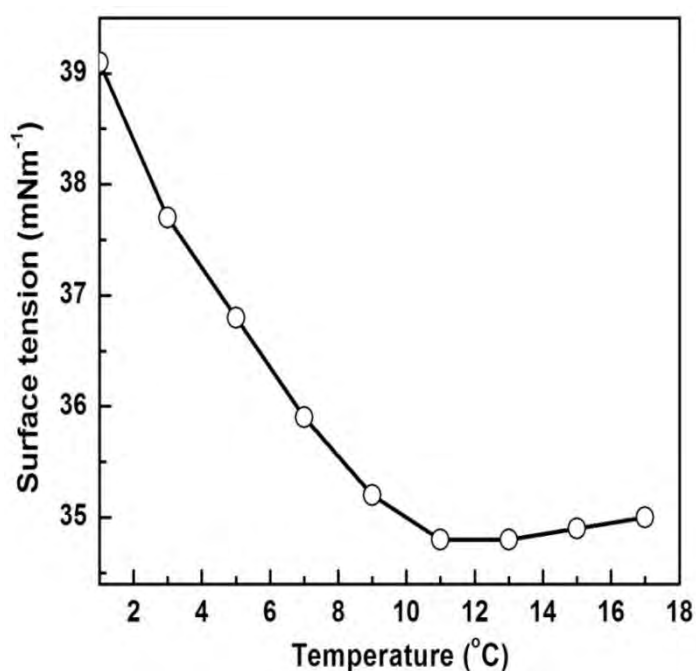
Figure 3.6: Surface tension of 3.64×10^{-3} M solution of TTAB at different temperatures

3.3 SURFACE EXCESS CONCENTRATION

The variation of surface excess concentration (Γ) of TTAB at different temperatures in pure water and in presence of NaCl is shown in Figure 3.7. At a definite temperature, the Γ value of TTAB was calculated from the slope of the straight line of the surface tension (γ) versus $\log_{10}C$ plot before CMC is reached with the help of the following equation [34].

$$\Gamma = -\frac{1}{2.303\,nRT}\left(\frac{\partial\gamma}{\partial lnC}\right)_{T,P} \tag{3.1}$$

Where R is the gas constant (8.314 $JK^{-1}mol^{-1}$), T is the absolute temperature, C is the surfactant concentration in the bulk and n is the number of species formed in the solution by the dissociation of the surfactant (for a non-ionic surfactant as there is no dissociation, n=1 and for a ionic surfactant in total dissociation, n=2). The percentage of error during the calculation of Γ values lies within ±1-2%. From Figure 3.7, it is clearly seen that for both TTAB in pure water and in presence of NaCl, increase in temperature cause a decrease in the Γ values. This decreasing trend of Γ values can be explained by taking into account the two considerations. At first, the dehydration of the hydrophilic head-group and at second, the thermal motion of the adsorbed molecules at the air-water interface. The head-group size shrinks due to the dehydration effect and that results in a close molecular packing in the adsorbed monolayer. On the other hand, disorganization of the adsorbed molecules at the air-water interface occurs with an increase in temperature as kinetic energy, thermal motion and chain flexibility increase [35,36]. Thus, the reason of lowering of Γ values with an increase in temperature can be expressed by these two opposing thermally controlled effects. With the increase of temperature van der Waals interactions among the alkyl chains become more and more unfavorable. Besides, an increase in temperature brings about perturbation in the adsorbed molecules. This results in a domination over the dehydration effect and a hindrance in the closer molecular packing of the monolayer at the air-water interface. As a consequence, the Γ value decreases with increasing temperature. Again, in the present work it is observed that the Γ values of TTAB in water are lower than the corresponding values in presence of NaCl in water. It can be explained as for solutions of ionic surfactants the adsorption of additional molecules as they migrate from the bulk of the solution to the air-water

interface is hindered by an electrostatic surface potential. This surface potential is electrostatically screened when an electrolyte is introduced to the surfactant solution [37,38]. As a result, the obstruction for further adsorption of surfactant molecules is substantially reduced, giving higher Γ values of TTAB in presence of NaCl.
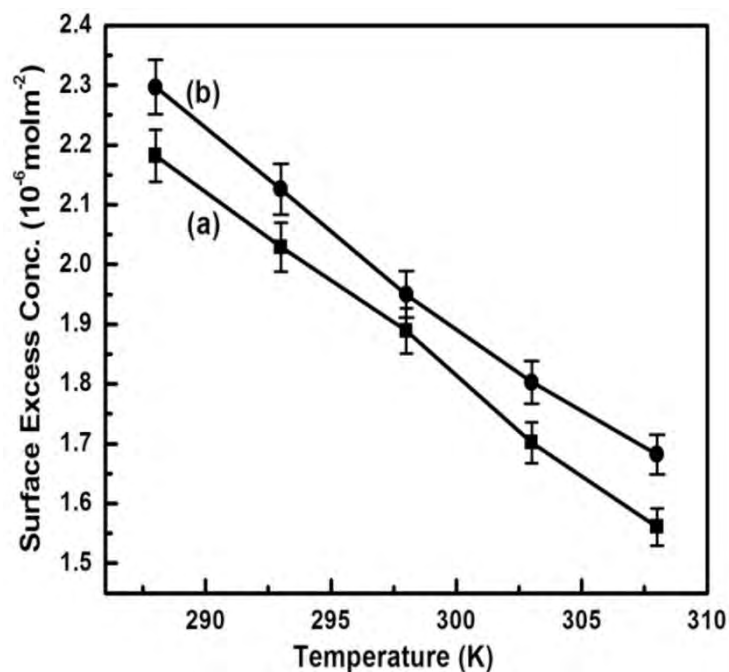
Figure 3.7: Surface excess concentration vs. temperature plot of TTAB in (a) pure water and (b) 0.0025 M NaCl solution

3.4 THERMODYNAMICS OF BULK MICELLIZATION AND SURFACE ADSORPTION

Table 3.3 and 3.4 shows the thermodynamic parameters involved in the micellization and adsorption of TTAB in water and in NaCl solution. The free energy (ΔG_m^0), entropy (ΔS_m^0) and enthalpy (ΔH_m^0) changes of micellization have been calculated using the following expressions [39,40].

$$\Delta G_m^0 = (1 + \beta)RT \ln X_{cmc} \qquad (3.2)$$

$$\Delta S_m^0 = -\left\{\frac{\partial(\Delta G_m^0)}{\partial T}\right\}_P \qquad (3.3)$$

$$\Delta H_m^0 = T\Delta S_m^0 + \Delta G_m^0 \qquad (3.4)$$

In presence of salt the following expression for free energy has been used:

$$\Delta G_m^0 = RT[\ln X_{CMC} + (1 - \alpha)\ln(X_{CMC} + X_s)] \qquad (3.5)$$

Where β denotes the degree of counter-ion binding, X_{cmc} denotes the mole fraction of the surfactant and X_s denotes the mole fraction of the salt at the CMC. The percentage of error during the calculation of thermodynamic parameters lies within ±2-3%.

Table 3.3: Thermodynamic parameters of adsorption and micellization* of Aqueous TTAB solution

Temp/K	ΔH_m^0/ kJmol⁻¹	ΔH_{ad}^0/ kJmol⁻¹	ΔS_m^0/ Jmol⁻¹K⁻¹	ΔS_{ad}^0/ Jmol⁻¹K⁻¹	ΔG_m^0/ kJmol⁻¹	ΔG_{ad}^0/ kJmol⁻¹
288	-0.675	16.742	136.176	257.308	-39.894	-57.363
293	-11.664	13.962	98.436	248.138	-40.506	-58.742
298	-22.79	11.489	60.696	238.968	-40.877	-59.723
303	-34.146	8.492	22.956	229.798	-41.102	-61.137
308	-45.68	5.907	-14.784	220.928	-41.127	-62.139

Table 3.4: Thermodynamic parameters of adsorption and micellization[*] of TTAB-0.0025 M NaCl solution

Temp/K	$\Delta H_m^o/$ kJmol^{-1}	$\Delta H_{ad}^o/$ kJmol^{-1}	$\Delta S_m^o/$ Jmol^{-1}K^{-1}	$\Delta S_{ad}^o/$ Jmol^{-1}K^{-1}	$\Delta G_m^o/$ kJmol^{-1}	$\Delta G_{ad}^o/$ kJmol^{-1}
288	-8.468	27.494	107.024	291.904	-39.291	-56.574
293	-15.016	16.712	84.264	254.194	-39.705	-57.767
298	-21.837	5.373	61.504	216.484	-40.165	-59.139
303	-28.611	-5.926	38.744	178.774	-40.35	-60.095
308	-35.58	-17.388	15.984	141.064	-40.503	-60.836

[*]The CMC values were taken in mole fractions for the calculation of the thermodynamic parameters

It can be seen from Table 3.3 and Table 3.4 that at all temperatures the free energy terms for micellization (ΔG_m^0) of TTAB in water and in the presence of NaCl are negative. These negative ΔG_m^0 values indicate that the transfer of alkyl chain of surfactant from aqueous solution to the micelle core (i.e., micelle formation) is a spontaneous process [41]. The ΔH_m^0 values of TTAB in pure water as well as in presence of NaCl are found to be negative within the studied temperature range. These values become more negative with increasing temperature. When a substantial number of water molecules surrounding the tiny hydrophilic head group become more important than the destruction of the iceberg around the alkyl chain then a negative ΔH_m^0 value can arise [41,42]. Again, a negative ΔH_m^0 value can be taken as the evidence of the London dispersion force, a major attractive force for micellization which become more and more dominant with increasing hydrocarbon chain length [43]. The hydrogen bond among the water molecules is diminished as the temperature increases [35,44] and therefore, to break up the iceberg structure around hydrophobic alkyl chains less energy is required. Therefore, ΔH_m^0 values become more negative with increasing temperature. Again, ΔS_m^0 values show a decreasing trend with increasing temperature for pure TTAB as well as in presence of NaCl. All ΔS_m^0 values are positive in presence of NaCl. On the contrary, for pure TTAB, ΔS_m^0 values successively decrease with temperature and finally become negative. The positive ΔS_m^0 value indicates that the micellization is governed by the entropy gain associated with the destruction of the iceberg around the hydrophobic alkyl chain [41]. A negative entropy change arises probably because of the ordering of randomly oriented monomeric units in a micellar structure, which outweighs the disordering effect of the

destruction of icebergs around the alkyl chains. With increasing temperature disordering of water molecules becomes less pronounced due to the destruction of the iceberg structure around the alkyl chain. That is why ΔS_m^0 shows a decreasing trend with increasing temperature.

Table 3.3 and 3.4 also list the thermodynamic parameters of adsorption of TTAB in pure state and in presence of NaCl. To calculate the change in free energy of adsorption(ΔG_{ad}^0), the following expression [33,41,45] is used:

$$\Delta G_{ad}^0 = \Delta G_m^0 - (\pi_{cmc}/\Gamma_{max}) \tag{3.6}$$

Where π_{cmc} denotes the equilibrium surface pressure and Γ_{max} denotes the maximum surface concentration of the adsorbed surfactant molecules at and above the CMC. ΔH_{ad}^0 and ΔS_{ad}^0 values were calculated from the equations similar to 3.3 and 3.4. The energy needed to transfer 1 mole of surfactant from solution to the surface at unit surface pressure is known as the free energy of adsorption [41]. It can be seen from Table 3.3 and 3.4 that all ΔG_{ad}^0 values are negative. It indicates the spontaneity of the adsorption process. ΔG_{ad}^0 values become more negative with increasing temperature which indicates more spontaneity. This is consistent with the fact that with increasing temperature dehydration of the head groups increases and it results in the increase in the hydrophobicity of the molecules [35]. It can also be seen that in the studied temperature range, ΔG_{ad}^0 value at a given temperature is more negative than the corresponding ΔG_m^0 value. It reflects a preference for adsorption than micelle formation and can be explained with the consideration that when micelles are formed, work has to be done to transfer the monomeric surfactant molecules from the surface to the micellar state in the bulk through the solvent medium.

In the present study all ΔS_{ad}^0 values are found to be positive and show a decreasing trend with increasing temperature in the studied temperature range. There is always a competition between the following two factors that controls the value of ΔS_{ad}^0: A positive ΔS_{ad}^0 value can arise from the destruction of the ordered ice-berg structure around the hydrophobic alkyl chain and the subsequent dangling of the alkyl chains of the adsorbed surfactant molecules at the air-water interface [46]. On the other hand, a negative ΔS_{ad}^0 value can arise from the spontaneous adsorption of the surfactant molecules in the form of organized monolayer and the concomitant loss of one degree of rotational freedom of the adsorbed molecules at the air-water interface [47]. With

increasing temperature iceberg structure is destroyed increasingly and it results in a successive domination of the second effect over the first one. As a result, ΔS_{ad}^0 values show a decreasing trend with increasing temperature.

In the present study the ΔH_{ad}^0 values of TTAB in pure water and in presence of NaCl at different temperatures have been calculated. It has been observed that in case of TTAB in pure water all ΔH_{ad}^0 values are positive and show a decreasing trend and in presence of NaCl the initial ΔH_{ad}^0 values are positive, show a decreasing trend and the last two values of ΔH_{ad}^0 become negative. At low temperatures, the surfactant remains much more hydrated and it needs more energy to adsorb at air-water interface and it reflects in the initial higher positive values of ΔH_{ad}^0. At higher temperatures, the surfactant is less hydrated and requires less energy to adsorb at the air-water interface and thereby ΔH_{ad}^0 values show a decreasing trend and tend to become negative with increasing temperature.

The entropy-enthalpy compensation plots for surface adsorption and bulk micellization of TTAB in pure water and in presence of NaCl are shown in Figures 3.8-3.11. An anticipated linear relationship is observed for both micelle and monolayer formation as shown in the figures below.
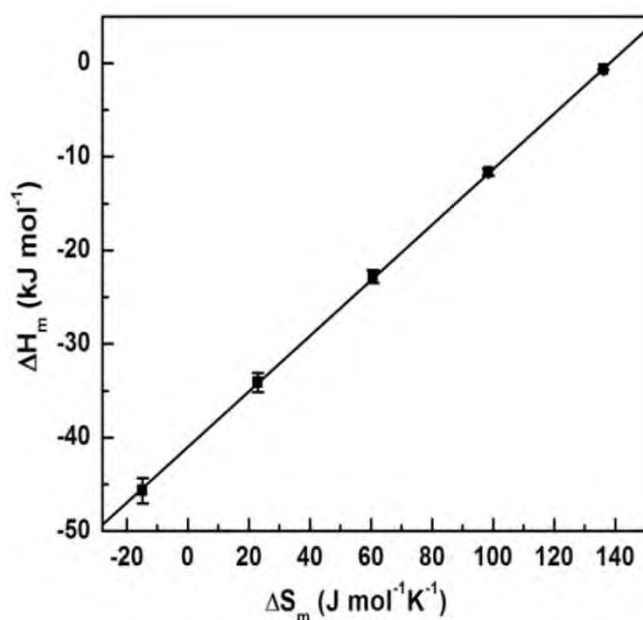
Figure 3.8: Enthalpy-entropy compensation plot for micellization of TTAB in aqueous solution
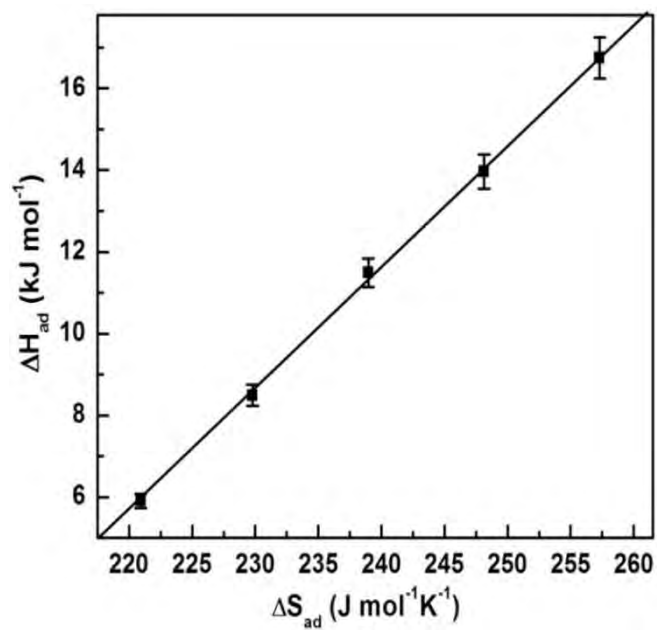
Figure 3.9: Enthalpy-entropy compensation plot for surface adsorption of TTAB in aqueous solution
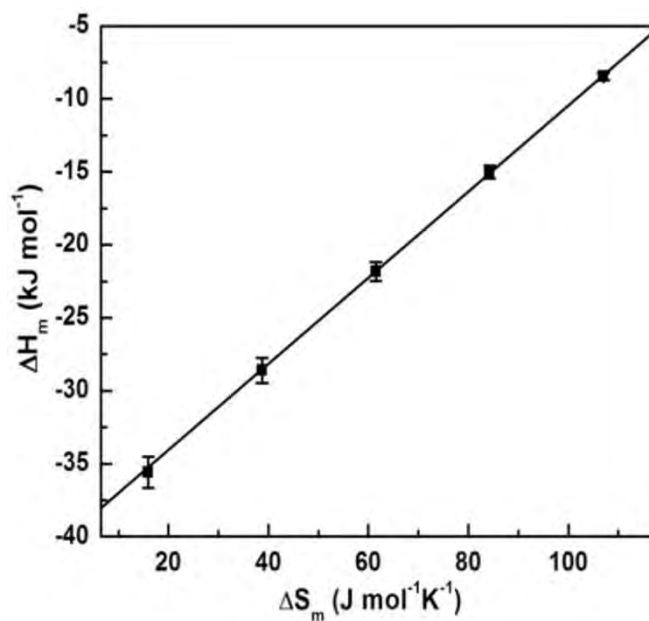
Figure 3.10: Enthalpy-entropy compensation plot for micellization of TTAB in 0.0025 M NaCl solution
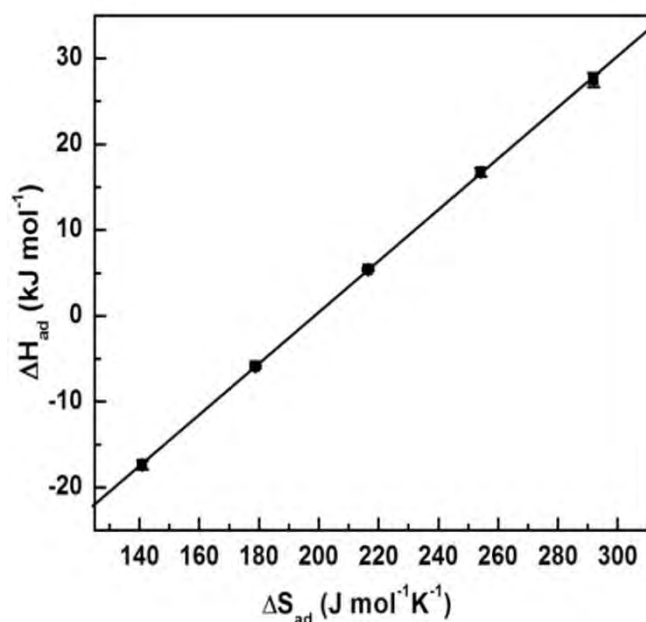
Figure 3.11: Enthalpy-entropy compensation plot for surface adsorption of TTAB in 0.0025 M NaCl solution

The compensation phenomenon between the entropy and enthalpy change for the surface adsorption and bulk micellization can be described in the form of

$$\Delta H^0_{m/ads} = \Delta H^*_{m/ads} + T_c \Delta S^0_{m/ads}$$

Where the intercept ($\Delta H^*_{m/ads}$) gives the information about the solute-solute interaction [30]. The slope, T_c in Kelvin, known as the compensation temperature, can be interpreted as a characteristic of solute-solute and solute-solvent interactions. Galan J.J. and Rodriguez J.R. carried out thermodynamic study of micellization of long chain alkyl pyridinium salts in aqueous solution and reported that the value of T_c is a measure of desolvatation of the chain of surfactant molecule and ΔH^0_m is a measure of the aggregation of the chains to make up the micelle [48]. It was found in the previous report that the T_c lies in a relatively narrow range from about 250 to 315K, for all processes involving aqueous solution of small molecules and physiological processes [49]. The T_c values for surface adsorption and bulk micellization of TTAB in pure water and in presence of NaCl are given in Table 3.5. The T_c values obtained in the present study are found to lie within the suggested literature values [50-52]. When the entropy term contributes less to the free energy, its counterpart, the enthalpy term contributes more to keep the negative free energy

nearly constant. This kind of behavior has been observed for aqueous solutions of ionic surfactants previously [50-52].

Table 3.5: Compensation temperature (T_c) values for TTAB in pure water and in 0.0025 M NaCl solution

System	Process	Compensation temperature (T_c)/K
TTAB in pure water	Adsorption	297.9
	Micellization	298.1
TTAB-0.0025M NaCl	Adsorption	298.1
	Micellization	298.0

3.5 SOLUBILIZATION STUDY OF SUDAN II WITH AQUEOUS TTAB AND TTAB-0.0025 M NaCl SOLUTION

In the present work, the solubilization study of sudan II in aqueous TTAB solution and in TTAB-0.0025 M NaCl solution was carried out. Figure 3.12 and 3.13 show the absorption spectra of sudan II in aqueous TTAB solution and in TTAB-0.0025 M NaCl solution. The concentration range of TTAB chosen to carry solubilization study in aqueous TTAB solution is from 1.5 mM to 6.5 mM and in TTAB-0.0025 M NaCl solution is from 1.5 mM to 6 mM. The solubilization studies were carried out with a fixed amount of dye in order to ensure solubilization equilibrium of the dye with the surfactant micelles. It can be seen from Figure 3.14 and 3.15 that below the CMC no significant absorbance was found, this indicates that hydrophobic natured sudan II is only solubilized in the hydrophobic environment of TTAB micelle. It can also be seen from Figure 3.14 and 3.15 that above the CMC the absorbance increases with increasing the TTAB concentration. The number of micelle increases with increasing TTAB concentration and therefore higher amount of sudan II molecules are taken up by the increased number of micelles. This observation is consistent with the previous observations [53].

It needs to be mentioned here that the CMC values of TTAB in aqueous solution and in presence of NaCl are decreased in presence of sudan II. It was reported by S.S. Shah et al. that the addition of organic additives affects the formation of micelles in aqueous surfactant solutions [54]. It was previously reported that the addition of alcohols to ionic surfactant solutions depresses the CMC of the surfactant [55-59]. Our present study is consistent with these observations. Schick [60] proposed that those molecules that are effective in reducing the CMC are solubilized in the outer portion of the micelle core and are under lateral pressure, tending to force them into the inner portion of the micelle. Islam M.N. et al. reported that water insoluble dye interacts with the micelles through the electrostatic attraction of the π-electron present in the aromatic ring of the dye to the cationic head of the surfactant in the micelle surface [41]. The dye molecules are thereby incorporated into the palisade layer of the micelle resulting in screening the micelle surface charge and thereby close packing of headgroups with a lowering of CMC. In the present case, some of the Sudan II molecules may solubilize in the palisade layer of the TTAB micelles which screens

the surface charge and consequent closer packing of the headgroups resulting in lowering of the CMC.
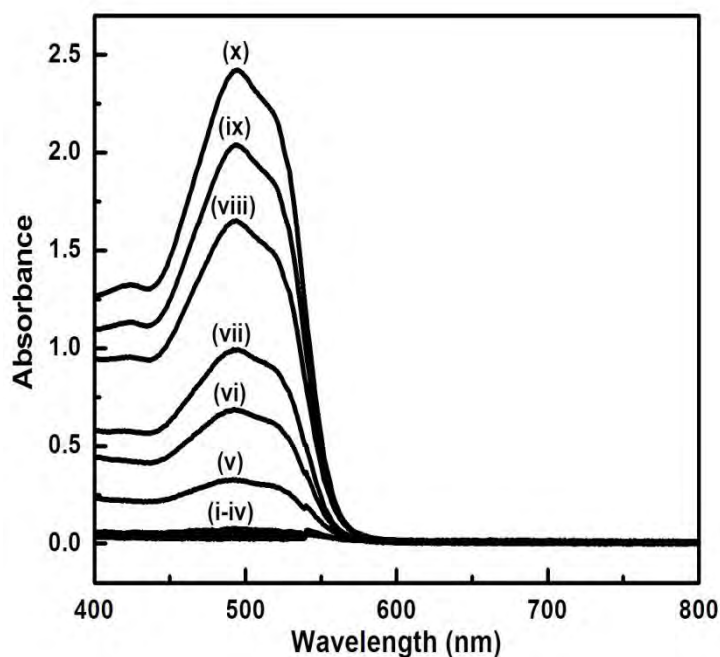
Figure 3.12: Absorption spectra of sudan Ⅱ in aqueous TTAB solution with TTAB concentrations below the CMC (i-iv), around and above the CMC: (v) 3.5 mM, (vi) 4 mM, (vii) 4.5 mM, (viii) 5.5 mM, (ix) 6 mM and (x) 6.5 mM
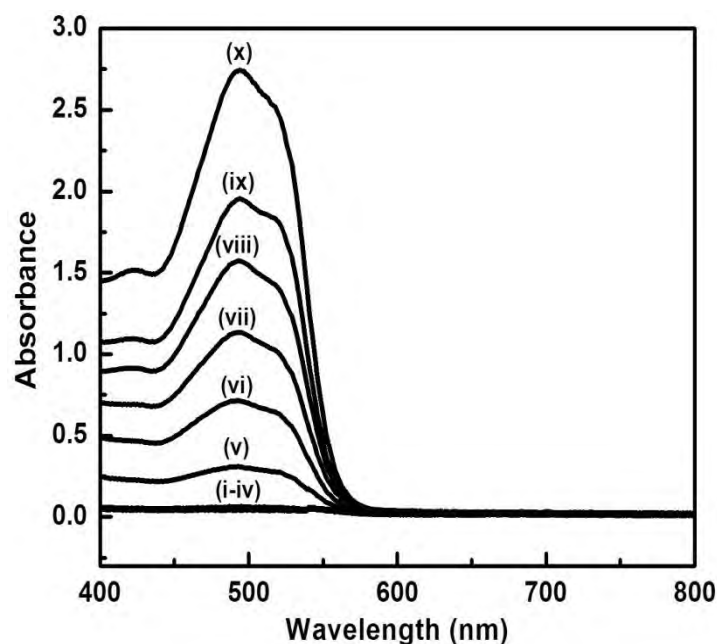
Figure 3.13: Absorption spectra of sudan Ⅱ in TTAB-0.0025 M NaCl solution with TTAB concentrations below the CMC (i-iv), around and above the CMC: (v) 3 mM, (vi) 3.5 mM, (vii) 4 mM, (viii) 4.5 mM, (ix) 5 mM and (x) 6 mM
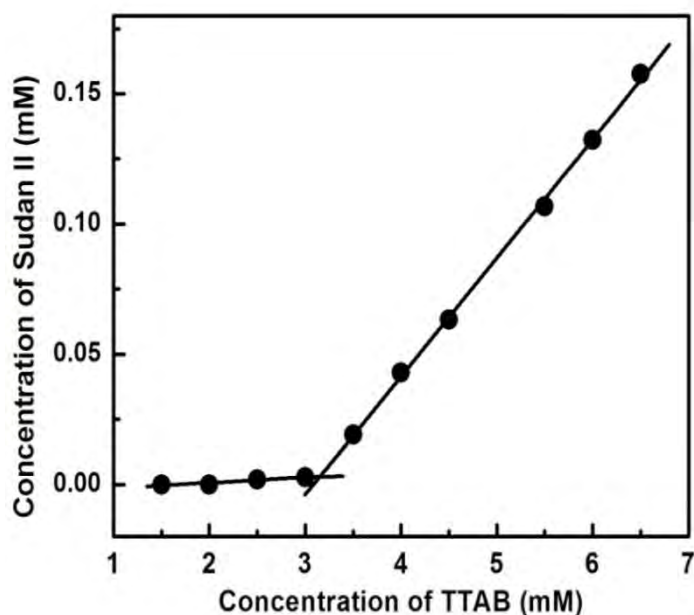
Figure 3.14: Solubilization of sudan II in aqueous TTAB solution of different concentrations
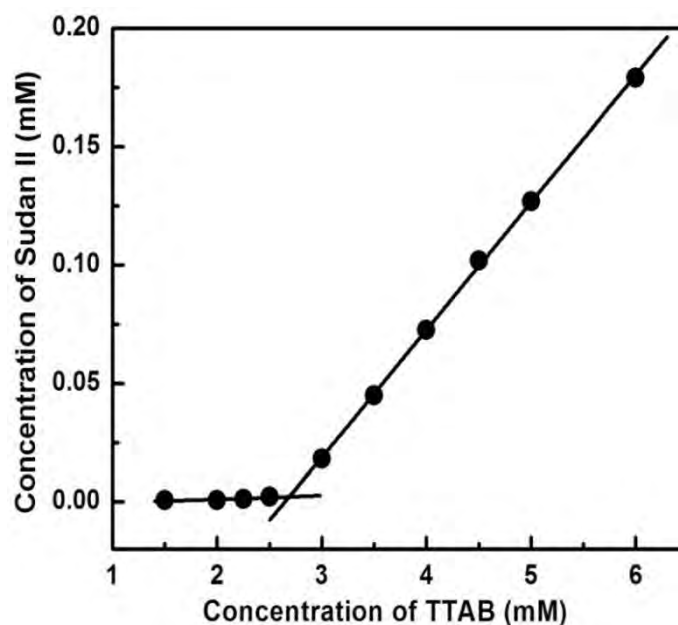
Figure 3.15: Solubilization of sudan II in aqueous TTAB solution of different concentrations in the presence of 0.0025 M NaCl solution

As the sudan II molecules are solubilized in the micellar aggregates, a small and gradual red shift of λ_{max} was observed. Around the CMC of TTAB in pure water, λ_{max} was found to be 492 nm and with the increase of concentration of TTAB, the λ_{max} is shifted to 495 nm for 6.5 mM solution. In presence of NaCl, this red shift of λ_{max} is very negligible and the shift is from 493 nm (around CMC) to 494 nm (6 mM). The

red shift of λ_{max} is an indication of the solubilization of sudan II molecules into the oil-like environment of the micellar core. This type of observation of red shift for solubilization of hydrophobic dyes in cationic and anionic surfactant micelles is in consistent with the previous studies of Islam M.N. et al. and Awan M.A. et al [41,61].

The effectiveness of a surfactant to solubilize a given solubilizate can be quantified by a term known as the molar solubilization ratio (MSR). The definition of this term can be given as the moles of hydrophobic compound solubilized by one mole of surfactant in the aqueous solution [62]. MSR can be determined from the slope of the plot of solute concentration against surfactant concentration above the CMC. The MSR values of TTAB in pure water and in presence of 0.0025 M NaCl are given in Table 3.6. It is seen from the Table 3.6 that MSR value is higher in presence of NaCl than that of in pure water. This is an indication of the better solubilizing power of TTAB in presence of NaCl. Because of the presence of counter-ions, the electrostatic repulsion between the charged headgroups at the micelle surface is greatly reduced. This results in a decrease in the surface area of the head group with a consequent decrease in CMC. Thus, the presence of counter-ions imparts an increase in the micellar aggregation number which results in an increase in the solubilization capacity [63,64].

Table 3.6: Molar solubilization ratio (MSR) values of sudan II in aqueous TTAB and TTAB-0.0025 M NaCl solution

Surfactant	NaCl concentration (M)	Regression coefficient (R^2)	MSR
TTAB	0.0000	0.9988	0.04553
TTAB	0.0025	0.9995	0.05377

REFERENCES

1. Islam, M.N.; Sarker, K.C.; Sharker, K.K.; *J. Surfact. Deterg.* 18, 9, **2015**

2. Islam, M.N.; Sharker, K.K.; Sarker, K.C.; *J. Surfact. Deterg.* 18, 651, **2015**

3. Tsujii, K.; Mino, J.; *J. Phys. Chem.* 82, 1610, **1978**

4. Chu, Z.; Feng, Y.J.; *Langmuir* 28, 1175, **2012**

5. Shinoda, K.; Yamaguchi, N.; Carlsson, A; *J. Phys. Chem.* 93, 7216, **1989**

6. Sharma, K.S.; Patil, S.R.; Rakshit, A.K.; Glenn, K.; Doiron, M.; Palepu, R.M.; Hassan, P.A.; *J. Phys. Chem. B* 108, 12804, **2004**

7. Pegram, L.M.; Record, M.T.J.; *J. Phys. Chem.* 111, 5411, **2007**

8. Lund, M.; Vacha, R.; Jungwirth, P.; *Langmuir* 24, 3387, **2008**

9. Islam, M.N.; Sarker, K.C.; Aktaruzzaman, G.; *J. Surfact. Deterg.* 17, 525, **2014**

10. Zhang, Y.; Cremer, P.S.; *Annu. Rev. Phys. Chem.* 61, 63, **2010**

11. dos Santos, A.P.; Dieh, A.; Levin,Y.; *Langmuir* 13, 10778, **2010**

12. Collins, K.D.; *Biophys. Chem.* 167, 43, **2012**

13. Zhang, Y.; Furyk, S.; Bergbreiter, D.E.; Cremer, P.S.; *J. Am. Chem. Soc.* 127, 14505, **2005**

14. Collins, K.D.; Neilson, G.W.; Enderby, J.E.; *Biophys. Chem.* 128, 95, **2007**

15. Heyda, J.; Lund, M.; Milan, O.; Slavicek, P., Jungwirth, P.; *J. Phys. Chem. B* 114, 10843, **2010**

16. van Beek, W.; Mandel, M.; *J. Chem. Soc. Faraday Trans* 74, 2339, **1978**

17. Zhang, Y.; Cremer, P.S.; *Proc. Nat. Aca. Sci.* 106, 15249, **2009**

18. Marcus, Y.; *Chem. Rev.* 109, 1346, **2009**

19. Endom, L.; Hertz, H.G.; Thul, B.; Zeidler, M.D.; *Dtsch. Bunsenges Phys. Chem.* 71, 1008, **1967**

20. Glasstone, S.; *Thermodynamics for Chemists*, 3rd edn, Litton Educational Publishing Inc, New York, **1947**

21. Chen, X.; Sarah,C.; Flores, S.C.; Lim, S-M; Zhang, Y.; Yang, T.; Kherb, J.; Cremer, P.S.; *Langmuir* 26, 16447, **2010**

22. Ropers, M.H.; Czichocki, G.; Brezesinski, G.; *J. Phys. Chem. B* 107, 5281, **2003**

23. Mata, J.; Varade, D.; Bahadur, P.; *Thermochim Acta* 428, 147, **2005**

24. Bojan, S.; Marija, B-R; *J. Colloid Interf. Sci* 338, 216, **2009**

25. Carolina, V.G.; Bales, B.L.; *J. Phys. Chem. B.* 107, 5398, **2003**

26. Moulik, S.P.; Haque, M.E.; Jana, P.K.; Das, A.R.; *J. Phys. Chem.* 100, 701, **1996**

27. Michele, A.D.; Brinchi, L.; Profio, P.D.; Germani, R.; Sawelli, G.; Onori, G.; *J. Colloid Interface Sci.* 358, 160, **2011**

28. Mata, J.; Varade, D.; Bahadur, P.; *Thermochim Acta* 428, 147, **2005**

29. Mukerjee, P.; Mysels, K.; Kapauan, J.; *J. Phys. Chem.* 71, 4166, **1967**

30. Abezgauz, L.; Kuperkar, K.; Hassan, P.A.; Ramon, O.; Bahadur, P.; Danino, D.; *J. Colloid Interface Sci.* 342, 83, **2010**

31. Srinivasan, V.; Blankschtein, D.; *Langmuir* 19, 9946, **2003**

32. Onoratoa, R.M.; Ottena, D.E.; Saykallya, R.J.; *Proc. Nat. Aca. Sci.* 106, 15176, **2009**

33. Islam, M.M.; Rahman, M.R.; Islam, M.N.; *International Journal of Scientific & Engineering Research.* 6, 1508, **2015**

34. Mukherjee, I.; Moulik, S.P.; Animesh, K.; *J. Colloid and Interf. Sci.* 394, 329, **2013**

35. Islam, M.N.; Kato, T.; *Langmuir* 19, 7201, **2003**

36. Crook, E.H.; Trebbi, G.F.; Fordice, D.B.; *J. Phys. Chem.* 68, 3592, **1964**

37. Chotipong, A.; Scamehorn, J.F.; Rirksomboon, T.; Chavadej, S.; Supaphol,P.; *Colloids and Surfaces* A*: Physicochem. Eng.* 297, 163, **2007**

38. Ritacco, H.; Langevin, D.; Diamant, H.; Andelman, D.; *Langmuir* 27, 1009, **2011**

39. Perger, T.M.; Rogac, M.B.; *J. Colloid and Interf. Sci.* 313, 69, 288, **2007**

40. Hribar, B.; Southall, N.T.; Vlachy, V.; Dill, K.A.; *J. Am. Chem. Soc.* 124, 12302, **2002**

41. Roy, J.C.; Islam, M.N.; Aktaruzzaman, G.; *J. Surfact. Deterg.* 17, 231, **2014**

42. Islam, M.N.; Kato, T.; *J. Phys. Chem. B* 107, 965, **2003**

43. Mosquera, V.; del Rio, J.M.; Attwood, D.; Garcia, M.; Jones, M.N.; Prieto, G.; Suarez, M.J.; Sarmiento, F.; *J. Colloid and Interf. Science* 206, 66, **1998**

44. Diamant, H.; Andelman, D.; *J. Phys. Chem.* 100, 13732, **1996**

45. Dahanayake, M.; Cohen, A.W.; Rosen, M. J.; *J. Phys Chem.* 90, 2413, **1982**

46. Callaghan, A.; Doyle, R.; Alexander, E.; Palepu, R.; *Langmuir* 9, 3422, **1993**

47. Mankowich, A.M.; *J. Am. Oil Chem. Soc* 42, 615, **1966**

48. Galan J.J.; Rodriguez J.R.; *J. Therm. Anal Calorim* 101, 359, **2010**

49. Lumry, R.; Rajender, S.; *Biopolymers* 9, 1125, **1970**

50. Lindman, B.; Brun, B.; *J. Colloid and Interf. Sci.* 42, 388, **1973**

51. Sugihara, G.; Hisatomi, M.; *J. Colloid and Interf. Sci.* 219, 31, **1999**

52. Kabir-Ud-Din; Koya, A.P.; Khan, Z.A.; *J. Colloid and Interf. Sci.* 342, 340, **2010**

53. Holmberg, K.; Jonsson, B.; Kronberg, B.; Lindman, B.; *Surfactant and Polymers in Aqueous Solution*, 2nd ed., Wiley, Chichester, **2003**

54. Shah, S.S.; Awan, M.A.; Ashraf, M.; Idris, S.A.; *Colloids and Surfaces A* 105, 319, **1995**

55. Shinoda, K.; *J. Phys. Chem.* 58, 1136, **1954**

56. Shirahama, K.; Kashiwabara, T.; *J. Colloid Interface Sci.* 36, 65, **1971**

57. Hayase, K.; Hayano, S.; *J. Colloid Interface Sci.* 63, 446, **1978**

58. Abu-Hamdiyyah, M.; *J. Phys. Chem.* 90, 1345, **1986**

59. Manabe, M.; Kawamura, H.; Sugihara, G.; Tanaka, M.; *Bull. Chem. Soc. Jpn.* 61, 1551, **1988**

60. Schick, M.J.; Fowkes, F.M.; *J. Phys. Chem.* 61, 1062, **1957**

61. Awan, M.A.; Shah, S.S.; *Colloids Surf. A* 122, 97, **1997**

62. Santanu, P.; Pak, K.Y.; *Ind. Eng. Chem. Res.* 45, 3552, **2006**

63. Harendra, S.; Vipulanandan, C.; *Ind. Eng. Chem. Res.* 50, 5831, **2011**

64. Schott, H.; *J. Phys. Chem.* 71, 3611, **1967**

CONCLUSION

In the present work, we have studied the influence of different electrolytes on the Krafft temperature (T_K) of TTAB in aqueous solution. The effect of different electrolytes of ionic strength 0.0025 on the critical micelle concentration (CMC) of TTAB at 25°C has also been studied. The adsorption and bulk micellar behavior of TTAB in aqueous and 0.0025 M NaCl solution at different temperatures have also been studied. Finally, the solubilization study of sudan II in aqueous TTAB and 0.0025 M NaCl solution has been carried out. It was observed that the T_K can be successfully modulated to lower and higher values in presence of different electrolytes. Less chaotropic NO_3^- and Cl^- as well as kosmotropic SO_4^{2-} and to some extent F^- decrease the T_K of TTAB. As kosmotropic SO_4^{2-} and F^- being strongly hydrated, do not want to lose their hydration shell to form contact ion pairs with the chaotropic TTAB headgroups. Therefore, in presence of these ions dispersion of surfactant molecules occurs which results in a decrease in T_K. Less chaotropic NO_3^- and Cl^- increase the activity of free water molecules and thereby hydration of TTAB molecules increase and it results in the decrease of T_K. On the other hand, more chaotropic SCN^- and I^- and to some extent Br^- increase the T_K. The T_K of TTAB slightly increases in presence of Br^- because of common ion effect. More chaotropic SCN^- and I^- form contact ion pair with the tetradecyltrimethylammonium ion due to their matching water affinities. Therefore, a reduction in the electrostatic repulsion between the surfactant ions occurs. It results in a consequent decrease in the solubility with a consequent increase in T_K. It is confirmed from the CMC study that the CMC of TTAB decreases in presence of all the electrolytes used. The decrease in CMC is due to the screening of the micelle surface charge by the associated counterions with a consequent closer packing of the surfactant molecules. It appears from the study that SO_4^{2-} being most effective in lowering the CMC of TTAB and propensity follows the order: SO_4^{2-} > NO_3^- > Br^- > Cl^- > F^- with F^- being least effective in lowering the CMC. In order to investigate the adsorption and bulk micellar behavior of TTAB the thermodynamic parameters of TTAB in aqueous and 0.0025 M NaCl solution at a temperature range varying from 15 to 35°C have been calculated. Within the studied temperature range ΔG_m^0 and ΔG_{ad}^0 values are found to be negative indicating the spontaneity of the processes. Again, the ΔG_{ad}^0 value is found to be more negative than the respective ΔG_m^0 value and it is an indication of the more spontaneity of adsorption

compared to micellization. The increase in negative value of ΔH_m^0 and decrease in positive value of ΔS_m^0 indicate that solvophobic contribution decreases while the London dispersion force between the alkyl chains increases with the rise of temperature. The decreasing trend of ΔH_{ad}^0 can be attributed to the energy required to adsorb at the air-water interface decreases with increasing temperature. The ΔS_{ad}^0 values decrease with increasing temperature, which indicates that the disordering of the ice-berg structure around the alkyl chains becomes less pronounced with increasing temperature. The surface excess concentration (Γ) value for TTAB in pure water and in presence of NaCl decreases gradually with increasing temperature and that can be attributed to an increase in the thermal motion and chain flexibility of the adsorbed molecules at the air water interface. It is revealed from the solubilization study that CMC decreases in presence of sudan II. This is attributed to some Sudan II molecules may be incorporated into the palisade layer of the micelle by the electrostatic attraction between the π-electrons present in the aromatic ring of the dye and the cationic head of the surfactant in the micelle surface. Again, solubilization study reveals that molar solubilization ratio (MSR) increases in presence of NaCl. It is evident from this result that the presence of counterions reduces the electrostatic repulsion between the charged headgroups of the micelles that facilitates closer molecular packing and thereby increase the oil-like environment of the micelle core. Therefore, more sudan II molecules are solubilized in presence of NaCl compared to pure aqueous TTAB solution.

APPENDIX

Data of TTAB

Krafft temperature data

Table 1: Krafft temperature data for pure TTAB solution and TTAB-NaNO₃ solution

Pure TTAB (0.0075 M)		TTAB (0.0075 M)-NaNO₃			
		0.001 M NaNO₃		0.0025 M NaNO₃	
Temperature (^{o}C)	Specific conductance (μS/cm)	Temperature (^{o}C)	Specific conductance (μS/cm)	Temperature (^{o}C)	Specific conductance (μS/cm)
2.0	329	2.0	440	2.0	619
2.5	329	2.5	439	2.5	619
3.0	329	3.0	438	3.0	619
3.5	330	3.5	438	3.5	620
4.0	331	4.0	437	4.0	621
4.5	332	4.5	437	4.5	625
5.0	333	5.0	437	5.0	632
5.5	335	5.5	440	5.5	640
6.0	338	6.0	444	6.0	649
6.5	340	6.5	449	6.5	658
7.0	342	7.0	455	7.0	668
7.5	344	7.5	461	7.5	676
8.0	347	8.0	468	8.0	677
8.5	350	8.5	477	8.5	677
9.0	354	9.0	487	9.0	677
9.5	358	9.5	497	9.5	677
10.0	367	10.0	505	10.0	676
10.5	382	10.5	512	10.5	676
11.0	419	11.0	512	11.0	675
11.5	444	11.5	512	11.5	675
12.0	445	12.0	511	12.0	674
12.5	446	12.5	510	12.5	674
13.0	445	13.0	509	13.0	673
13.5	444	13.5	508		
14.0	443	14.0	507		
14.5	443	14.5	506		
15.0	443	15.0	505		
15.5	443	15.5	504		
16.0	442				
16.5	442				
17.0	441				

Table 2: Krafft temperature data for TTAB-Na₂SO₄ solution

TTAB (0.0075 M)-Na₂SO₄					
Na₂SO₄ (ionic strength= 0.001)		Na₂SO₄ (ionic strength= 0.0025)		Na₂SO₄ (ionic strength= 0.005)	
Temperature (^{o}C)	Specific conductance (μS/cm)	Temperature (^{o}C)	Specific conductance (μS/cm)	Temperature (^{o}C)	Specific conductance (μS/cm)
2.0	407	2.0	547	1.0	804
2.5	407	2.5	547	1.5	804
3.0	407	3.0	547	2.0	804
3.5	408	3.5	547	2.5	804
4.0	409	4.0	547	3.0	804
4.5	412	4.5	548	3.5	805
5.0	415	5.0	548	4.0	806
5.5	418	5.5	549	4.5	810
6.0	422	6.0	552	5.0	815

6.5	426	6.5	558	5.5	820
7.0	430	7.0	564	6.0	826
8.0	439	7.5	569	6.5	831
8.5	444	8.0	575	7.0	837
9.0	449	8.5	581	7.5	842
9.5	454	9.0	589	8.0	847
10.0	459	9.5	590	8.5	849
10.5	465	10.0	591	9.0	849
11.0	470	10.5	591	9.5	849
11.5	470	11.0	591	10.0	848
12.0	470	11.5	591	10.5	848
12.5	470	12.0	590	11.0	847
13.0	469	12.5	590	11.5	847
13.5	469	13.0	590	12.0	846
14.0	468			12.5	846
14.5	468				
15.0	468				

Table 3: Krafft temperature data for TTAB-NaCl solution

TTAB (0.0075 M)-NaCl					
0.001 M NaCl		0.0025 M NaCl		0.005 M NaCl	
Temperature (^{o}C)	Specific conductance (μS/cm)	Temperature (^{o}C)	Specific conductance (μS/cm)	Temperature (^{o}C)	Specific conductance (μS/cm)
2.0	482	1.5	693	2.5	942
2.5	481	2.0	692	3.0	941
3.0	480	2.5	691	3.5	941
3.5	479	3.0	691	4.0	941
4.0	478	3.5	692	4.5	942
4.5	476	4.0	693	5.0	944
5.0	475	4.5	696	5.5	950
5.5	475	5.0	700	6.0	957
6.0	475	5.5	706	6.5	968
6.5	474	6.0	712	7.0	979
7.0	475	6.5	718	7.5	983
7.5	475	7.0	725	8.0	983
8.0	477	7.5	734	8.5	982
8.5	478	8.0	744	9.0	981
9.0	480	8.5	756	9.5	980
9.5	485	9.0	770	10.0	979
10.0	495	9.5	781	10.5	979
10.5	511	10.0	788	11.0	978
11.0	527	10.5	789		
11.5	542	11.0	788		
12.0	543	11.5	788		
12.5	543	12.0	786		
13.0	543	12.5	785		
13.5	542	13.0	784		
14.0	542	13.5	784		
14.5	541	14.0	784		
15.0	541	14.5	784		
15.5	541				

Table 4: Krafft temperature data for TTAB-NaF solution

TTAB (0.0075 M)-NaF							
0.001 M NaF		0.0025 M NaF		0.005 M NaF		0.0075 M NaF	
Temp. (^{o}C)	Specific conductance (μS/cm)	Temp. (^{o}C)	Specific conductance (μS/cm)	Temp. (^{o}C)	Specific conductance (μS/cm)	Temp. (^{o}C)	Specific conductance (μS/cm)
4.5	447	4.5	614	3.0	839	4.0	1091
5.0	446	5.0	612	3.5	838	4.5	1091
5.5	445	5.5	610	4.0	838	5.0	1091
6.0	443	6.0	608	4.5	837	5.5	1092
6.5	442	6.5	607	5.0	836	6.0	1093
7.0	442	7.0	607	5.5	836	6.5	1095
7.5	443	7.5	606	6.0	837	7.0	1098
8.0	444	8.0	607	6.5	840	7.5	1102
8.5	447	8.5	608	7.0	844	8.0	1107
9.0	450	9.0	611	7.5	848	8.5	1115
9.5	454	9.5	616	8.0	855	9.0	1123
10.0	463	10.0	634	8.5	867	9.5	1130
10.5	476	10.5	656	9.0	879	10.0	1138
11.0	505	11.0	677	9.5	891	10.5	1145
11.5	533	11.5	692	10.0	903	11.0	1153
12.0	534	12.0	693	10.5	913	11.5	1153
12.5	535	12.5	692	11.0	914	12.0	1153
13.0	534	13.0	692	11.5	914	12.5	1152
13.5	532	13.5	691	12.0	914	13.0	1152
14.0	531	14.0	689	12.5	913	13.5	1152
14.5	530	14.5	689	13.0	913	14.0	1151
15.0	530	15.0	688	13.5	912	14.5	1151
15.5	530	15.5	687	14.0	912	15.0	1151
16.0	530	16.0	686	14.5	912		
				15.0	911		

Table 5: Krafft temperature data for TTAB-NaBr solution

TTAB (0.0075 M)-NaBr							
0.001 M NaBr		0.0025 M NaBr		0.005 M NaBr		0.0075 M NaBr	
Temp. (^{o}C)	Specific conductance (μS/cm)	Temp. (^{o}C)	Specific conductance (μS/cm)	Temp. (^{o}C)	Specific conductance (μS/cm)	Temp. (^{o}C)	Specific conductance (μS/cm)
2.5	390	2.5	511	3.5	712	3.5	901
3.0	388	3.0	510	4.0	709	4.0	898
3.5	385	3.5	506	4.5	706	4.5	895
4.0	384	4.0	504	5.0	704	5.0	894
4.5	385	4.5	502	5.5	701	5.5	895
5.0	384	5.0	501	6.0	699	6.0	896
5.5	386	5.5	499	6.5	696	6.5	898
6.0	387	6.0	500	7.0	695	7.0	899
6.5	389	6.5	501	7.5	695	7.5	901
7.0	390	7.0	500	8.0	697	8.0	903
7.5	393	7.5	500	8.5	700	8.5	904
8.0	396	8.0	502	9.0	703	9.0	908
8.5	399	8.5	506	9.5	708	9.5	912
9.0	400	9.0	509	10.0	713	10.0	917
9.5	405	9.5	514	10.5	720	10.5	922
10.0	409	10.0	524	11.0	749	11.0	929
10.5	416	10.5	541	11.5	781	11.5	977
11.0	431	11.0	581	12.0	805	12.0	1024
11.5	466	11.5	610	12.5	803	12.5	1033
12.0	497	12.0	614	13.0	802	13.0	1032
12.5	503	12.5	614	13.5	801	13.5	1030
13.0	502	13.0	612	14.0	800	14.0	1029

Temp.	Spec. cond.	Temp.	Spec. cond.	Temp.	Spec. cond.	Temp.	Spec. cond.
13.5	502	13.5	611	14.5	799	14.5	1027
14.0	501	14.0	610	15.0	798	15.0	1026
14.5	500	14.5	610	15.5	797	15.5	1025
15.0	499	15.0	609	16.0	796	16.0	1024
15.5	499	15.5	609	16.5	796	16.5	1023
16.0	498	16.0	608	17.0	795	17.0	1022
16.5	499	16.5	607				
		17.0	606				
		17.5	606				

Table 6: Krafft temperature data for TTAB-NaSCN solution

TTAB (0.0075 M)-NaSCN							
0.001 M NaSCN		0.0025 M NaSCN		0.005 M NaSCN		0.0075 M NaSCN	
Temp. (^{o}C)	Specific conductance (μS/cm)	Temp. (^{o}C)	Specific conductance (μS/cm)	Temp. (^{o}C)	Specific conductance (μS/cm)	Temp. (^{o}C)	Specific conductance (μS/cm)
2.0	402	9.0	560	17.0	724	13.0	899
2.5	402	9.5	560	17.5	724	13.5	899
3.0	403	10.0	559	18.0	724	14.0	898
3.5	405	10.5	559	18.5	724	14.5	899
4.0	409	11.0	559	19.0	724	15.0	899
4.5	414	11.5	559	19.5	725	15.5	898
5.0	420	12.0	559	20.0	725	16.0	899
5.5	428	12.5	559	20.5	725	16.5	899
6.0	438	13.0	559	21.0	726	17.0	898
6.5	455	14.0	559	21.5	726	17.5	898
7.0	473	14.5	560	22.0	726	18.0	898
7.5	492	15.0	561	22.5	727	18.5	898
8.0	499	16.0	564	23.0	729	19.0	899
8.5	502	17.0	567	23.5	731	19.5	900
9.0	502	17.5	569	24.0	733	20.0	901
9.5	501	18.0	571	24.5	735	20.5	902
10.0	500	18.5	574	25.0	738	21.0	903
10.5	499	19.0	577	25.5	741	21.5	904
11.0	498	19.5	579	26.0	745	22.0	905
11.5	497	20.0	580	26.5	750	22.5	906
12.0	497	20.5	581	27.0	755	23.0	907
12.5	496	21.0	582	27.5	760	23.5	909
13.0	495	21.5	583	28.0	760	24.0	910
13.5	495	22.0	584	28.5	761	24.5	912
14.0	495	22.5	585	29.0	762	25.0	914
		23.0	586	29.5	762	25.5	916
		23.5	587	30.0	763	26.0	918
		24.0	588	30.5	763	26.5	920
				31.5	764	27.0	922
				32.0	764	27.5	925
				32.5	765	28.0	928
				33.0	765	28.5	932
						29.0	938
						29.5	944
						30.0	951
						30.5	960
						31.0	970
						31.5	976
						32.0	977
						32.5	978
						33.0	979
						33.5	980
						34.0	981
						34.5	981
						35.0	982

						35.5	982
						36.0	982
						36.5	983
						37.0	983

Table 7: Krafft temperature data for TTAB-NaI solution

TTAB (0.0075 M)-NaI			
0.001 M NaI		0.0025 M NaI	
Temperature (^{o}C)	Specific conductance (μS/cm)	Temperature (^{o}C)	Specific conductance (μS/cm)
3.0	399	8.0	499
3.5	398	8.5	499
4.0	396	9.0	499
4.5	394	9.5	498
5.0	394	10.0	498
5.5	392	10.5	498
6.0	393	11.0	498
6.5	392	11.5	498
7.0	390	12.0	498
7.5	390	12.5	497
8.0	390	13.0	497
8.5	390	13.5	497
9.0	391	14.0	497
9.5	390	14.5	497
10.0	391	15.0	497
10.5	391	15.5	498
11.0	391	16.0	499
11.5	392	16.5	500
12.0	392	17.0	501
12.5	392	17.5	502
13.0	392	18.0	503
13.5	394	18.5	504
14.0	395	19.0	506
14.5	395	19.5	507
15.0	395	20.0	508
15.5	396	20.5	510
16.0	397	21.0	512
16.5	399	21.5	513
17.0	400	22.0	516
17.5	402	22.5	519
18.0	406	23.0	521
18.5	414	23.5	526
19.0	426	24.0	530
19.5	444	24.5	534
20.0	459	25.0	539
20.5	476	25.5	543
21.0	487	26.0	546
21.5	488	26.5	549
22.0	490	27.0	553
22.5	491	27.5	557
23.0	492	28.0	561
23.5	493	28.5	565
24.0	493	29.0	569
24.5	494	29.5	574
25.0	494	30.0	579
25.5	495	30.5	584
26.0	496	31.0	589
26.5	497	31.5	594
27.0	498	32.0	598
27.5	499	32.5	602
28.0	500	33.0	606

28.5	501	33.5	611
29.0	502	34.0	616
		34.5	621
		35.0	626
		35.5	630
		36.0	631
		36.5	632
		37.0	633
		37.5	633
		38.0	634
		38.5	634
		39.0	635
		39.5	635
		40.0	636
		40.5	637
		41.0	637
		41.5	638
		42.0	638
		42.5	638
		43.0	639
		43.5	639
		44.0	640
		44.5	641
		45.0	641

Table 8: Krafft temperature of TTAB in presence of electrolytes at different ionic strengths

Ionic strength	Krafft temperature (ºC)						
	NaCl	Na_2SO_4	NaBr	NaI	NaSCN	$NaNO_3$	NaF
0.0000	11.6	11.6	11.6	11.6	11.6	11.6	11.6
0.0010	11.5	11.0	12.1	21.0	7.80	10.4	11.5
0.0025	9.90	9.20	11.7	35.5	19.4	7.60	11.4
0.0050	7.20	8.20	11.9	45.5	27.5		10.5
0.0075			12.1		31.5		11.0

Critical micelle concentration data

Conductrometric method

Table 9: Data of specific conductance vs. concentration of aqueous TTAB at different temperatures (288K, 293K, 298K, 303K, 308K)

Concentration (mM)	288K	293K	298K	303K	308K
	Specific conductance (μS/cm)	Specific conductance (μS/cm)	Specific conductance (μS/cm)	Specific conductance (μS/cm)	Specific conductance (μS/cm)
0.2941	29.2	27.7	28.9	27.6	28
0.5769	56.8	55.2	55.6	54.1	54.8
0.8490	82.6	79.6	81.4	79.9	80.1
1.1111	108	105.5	105.9	104.1	104
1.3636	131.8	128.3	129.4	128	127.8
1.6071	154.8	150.7	152	150.4	150.6
1.8421	177	173.7	173.7	171.9	172.2
2.0690	197.9	194.3	194.3	192.9	194
2.2881	212	210	211	209	209
2.5000	232	229	230	229	230
2.7050	251	248	249	248	248
2.9032	269	266	266	266	266

3.0952	288	283	284	283	283
3.2812	306	301	301	300	300
3.4615	320	316	317	316	316
3.6364	330	328	329	329	330
3.8060	338	336	337	340	343
3.9705	344	342	344	349	354
4.1304	349	347	350	355	360
4.2857	353	352	354	360	368
4.4366	357	356	358	364	373
4.5833	361	360	362	368	377
4.7260	364	363	366	372	381
4.8649	368	366	369	376	386
5.0000	371	369	373	379	389
5.1316	374	372	376	383	392
5.2597	377	375	379	387	395
5.3846	379	377	381	389	398
5.5063	381	379	384	391	403
5.6250	384	382	387	393	405

Table 10: Data of specific conductance vs. concentration of TTAB-0.0025 M NaCl solution at different temperatures (288K, 293K, 298K, 303K, 308K)

Concentration (mM)	288K Specific conductance (μS/cm)	293K Specific conductance (μS/cm)	298K Specific conductance (μS/cm)	303K Specific conductance (μS/cm)	308K Specific conductance (μS/cm)
0.2353	329	325	322	322	327
0.4615	351	346	342	341	347
0.6792	370	365	362	360	365
0.8889	388	384	380	380	385
1.0910	408	403	398	397	403
1.2857	426	422	416	414	420
1.4737	443	438	433	431	437
1.6552	460	454	449	448	453
1.8305	476	469	466	464	470
2.0000	492	485	481	479	486
2.1639	506	499	495	494	500
2.3226	522	515	509	508	513
2.4762	536	528	523	522	527
2.6250	549	542	536	536	541
2.7692	561	556	549	549	553
2.9091	573	567	561	561	567
3.0448	585	578	573	573	579
3.1765	595	588	582	583	590
3.3043	604	595	589	592	600
3.4286	608	601	597	598	609
3.5493	613	605	602	604	614
3.6667	617	609	606	609	619
3.7808	621	613	610	613	623
3.8919	624	616	613	617	628
4.0000	627	619	616	620	631
4.1053	629	621	618	622	635
4.2078	631	624	620	625	638
4.3077	634	626	623	627	640
4.4051	636	628	625	631	643
4.5000		630	627	634	647
4.5926		632	629	636	650
4.6829		634	631	638	652
4.7711				640	654
4.8571				643	656

Table 11: Data of specific conductance vs. concentration of TTAB in presence of NaNO$_3$, Na$_2$SO$_4$, NaF and NaBr at 25°C

NaNO$_3$		Na$_2$SO$_4$		NaF		NaBr	
Conc. (mM)	Specific conductance (μS/cm)	Conc. (mM)	Specific conductance (μS/cm)	Conc. (mM)	Specific conductance (μS/cm)	Conc. (mM)	Specific conductance (μS/cm)
0.2157	312	0.2353	226	0.2157	277	0.1961	243
0.4231	331	0.4615	246	0.4231	296	0.3846	260
0.6226	349	0.6792	266	0.6226	314	0.5660	278
0.8148	365	0.8889	285	0.8148	332	0.7407	293
1.0000	382	1.0909	303	1.0000	349	0.9091	308
1.1786	399	1.2857	321	1.1786	366	1.0714	324
1.3509	414	1.4737	338	1.3509	382	1.2281	337
1.5172	429	1.6552	354	1.5172	397	1.3793	352
1.6780	444	1.8305	369	1.6780	411	1.5254	365
1.8333	458	2.0000	385	1.8333	425	1.6667	377
1.9836	471	2.1639	400	1.9836	439	1.8033	389
2.1290	485	2.3226	412	2.1290	452	1.9355	402
2.2698	497	2.4762	423	2.2698	464	2.0635	413
2.4062	509	2.6250	431	2.4062	477	2.1875	424
2.5385	518	2.7692	437	2.5385	490	2.3077	435
2.6667	526	2.9091	443	2.6667	501	2.4242	446
2.7910	531	3.0448	447	2.7910	511	2.5373	456
2.9118	537	3.1765	451	2.9118	523	2.6470	466
3.0290	541	3.3043	455	3.0290	533	2.7536	475
3.1428	544	3.4286	458	3.1428	543	2.8571	483
3.2535	548	3.5493	461	3.2535	552	2.9577	488
3.3611	551	3.6667	464	3.3611	560	3.0556	494
3.4658	554	3.7808	467	3.4658	567	3.1507	499
3.5676	557	3.8919	470	3.5676	573	3.2432	504
3.6667	560	4.0000	472	3.6667	578	3.3333	507
3.7632	562			3.7632	582	3.4210	510
3.8571	565			3.8571	586	3.5065	513
3.9487	568			3.9487	590	3.5897	515
4.0380	570			4.0380	592	3.6709	517
4.1250	573			4.1250	594	3.7500	520
				4.2099	596	3.8272	522
				4.2927	599	3.9024	524
				4.3735	601	3.9759	526
				4.4524	604		
				4.5294	606		
				4.6046	608		

Surface tensiometric method

Table 13: Data of surface tension vs. logarithm of concentration of aqueous solution of TTAB at different temperatures (288K, 293K, 298K, 303K, 308K)

Log C	288K	293K	298K	303K	308K
	Surface tension (mN/m)	Surface tension (mN/m)	Surface tension (mN/m)	Surface tension (mN/m)	Surface tension (mN/m)
-3.365	57.6	56.9	56.5	55.5	54.9
-3.073	50.7	50.5	50.3	50.1	49.9
-2.905	46.7	46.4	46.3	46.5	46.4
-2.788	43.4	44.0	44.0	44.3	44.4
-2.699	41.5	41.6	42.0	42.3	42.5
-2.628	39.6	40.0	40.7	41.0	41.4
-2.568	38.3	38.7	39.2	39.7	40.3
-2.518	37.3	37.7	38.1	39.0	39.5
-2.474	36.2	36.7	37.4	38.1	38.6

-2.436	35.5	36.0	36.5	37.3	37.9
-2.402	35.4	35.8	36.4	37.1	37.6
-2.371	35.4	35.8	36.4	37.1	37.6
-2.343	35.3	35.8	36.4	37.1	37.5
-2.318	35.4	35.8	36.3	37.0	37.6
-2.294	35.4	35.8	36.4	37.1	37.5
-2.273	35.3	35.7	36.3	37.1	37.6
-2.253	35.4	35.8	36.4	37.0	37.6
-2.235	35.4	35.8	36.4	37.1	37.5
-2.218	35.4	35.7	36.4	37.1	37.5

Table 14: Data of surface tension vs. logarithm of concentration of TTAB-0.0025 M NaCl solution at different temperatures (288K, 293K, 298K, 303K, 308K)

Log C	288K	293K	298K	303K	308K
	Surface tension (mN/m)	Surface tension (mN/m)	Surface tension (mN/m)	Surface tension (mN/m)	Surface tension (mN/m)
-3.406	57.1	56.5	55.9	55.4	55.1
-3.114	49.9	49.5	49.2	49.3	49.1
-2.946	45.3	45.4	45.4	45.5	45.6
-2.829	42.8	42.9	43.1	43.3	43.6
-2.740	40.5	40.4	41.1	41.3	41.7
-2.669	38.6	38.9	39.3	40.0	40.2
-2.610	36.8	37.3	37.9	38.7	39.1
-2.559	35.8	36.4	36.9	37.5	38.1
-2.516	34.5	35.3	36.0	36.8	37.5
-2.477	34.1	34.6	35.3	36.0	36.6
-2.443	34.1	34.6	35.2	35.9	36.4
-2.412	34.0	34.5	35.2	35.9	36.4
-2.384	34.0	34.6	35.2	35.9	36.4
-2.359	34.1	34.6	35.1	35.8	36.3
-2.336	34.0	34.6	35.2	35.9	36.3
-2.314	34.0	34.5	35.2	35.9	36.4
-2.295	34.0	34.6	35.1	35.8	36.4
-2.276	34.1	34.5	35.2	35.9	36.3
-2.259	34.0	34.6	35.2	35.9	36.4

Table 15: Data of surface tension vs. logarithm of concentration of TTAB in presence of NaNO$_3$, Na$_2$SO$_4$, NaF and NaBr at 25°C

NaNO$_3$		Na$_2$SO$_4$		NaF		NaBr	
Log C	Surface tension (mN/m)	Log C	Surface tension (mN/m)	Log C	Surface tension (mN/m)	Log C	Surface tension (mN/m)
-3.406	56.1	-3.406	54.6	-3.310	53.8	-3.406	55.0
-3.114	48.0	-3.114	48.1	-3.017	48.1	-3.114	48.1
-2.946	43.4	-2.946	44.2	-2.849	44.8	-2.946	44.2
-2.829	40.5	-2.829	41.4	-2.732	42.7	-2.829	41.2
-2.740	38.0	-2.740	39.2	-2.643	41.1	-2.740	39.3
-2.669	35.9	-2.669	37.5	-2.572	39.4	-2.669	37.4
-2.610	34.2	-2.610	36.5	-2.513	38.4	-2.610	36.3
-2.559	33.7	-2.559	36.1	-2.462	37.7	-2.559	35.0
-2.516	33.6	-2.516	36.1	-2.419	37.7	-2.516	34.5
-2.477	33.7	-2.477	36.0	-2.380	37.6	-2.477	34.4
-2.443	33.7	-2.443	36.1	-2.346	37.7	-2.443	34.5
-2.412	33.6	-2.412	36.1	-2.315	37.7	-2.412	34.5
-2.384	33.7	-2.384	36.0	-2.287	37.6	-2.384	34.4
-2.359	33.7	-2.359	36.1	-2.262	37.7	-2.359	34.5
-2.336	33.6	-2.336	36.1	-2.239	37.6	-2.336	34.5
-2.314	33.7	-2.314	36.0	-2.217	37.7	-2.314	34.4
-2.295	33.7	-2.295	36.1			-2.295	34.5

Table 16: Data of surface excess concentration vs. temperature plots of TTAB in pure water and in presence of 0.0025 M NaCl solution

Temperature (K)	Surface excess concentration (10^{-6}molm^{-2})	
	TTAB in pure water	TTAB in 0.0025 M NaCl solution
288	2.182	2.297
293	2.029	2.126
298	1.889	1.950
303	1.702	1.803
308	1.561	1.682

Solubilization data

Table 17: Data of calibration curve of sudan Ⅱ in surfactant media

Amount of dye (g)	Absorbance
0.00000	0.000
0.00905	0.169
0.01810	0.316
0.03620	0.588
0.07240	1.137
0.09050	1.403
0.10860	1.695
0.11946	1.840
0.14480	2.237
0.18100	2.783
0.21720	3.299

Table 18: Data of surfactant concentration vs. absorbance of sudan Ⅱ in aqueous and in 0.0025 M NaCl solution

Pure TTAB		TTAB-0.0025 M NaCl	
Surfactant concentration (mM)	Absorbance	Surfactant concentration (mM)	Absorbance
1.5	0.028	1.50	0.042
2.0	0.033	2.00	0.042
2.5	0.061	2.25	0.050
3.0	0.075	2.50	0.064
3.5	0.323	3.00	0.309
4.0	0.682	3.50	0.712
4.5	0.992	4.00	1.134
5.5	1.648	4.50	1.574
6.0	2.038	5.00	1.954
6.5	2.421	6.00	2.743

Table 19: Data of surfactant concentration vs. dye concentration sudan Ⅱ in aqueous and in 0.0025 M NaCl solution

Pure TTAB		TTAB-0.0025 M NaCl	
Surfactant concentration (mM)	Dye concentration (mM)	Surfactant concentration (mM)	Dye concentration (mM)
1.5	5.56E-05	1.50	6.67E-04
2.0	5.56E-05	2.00	6.67E-04
2.5	0.00195	2.25	0.00122
3.0	0.00283	2.50	0.00211
3.5	0.01923	3.00	0.01828
4.0	0.04290	3.50	0.04490
4.5	0.06335	4.00	0.07268
5.5	0.10670	4.50	0.10180
6.0	0.13240	5.00	0.12680
6.5	0.15760	6.00	0.17890

CALCULATION

Micellization

Counter ion binding calculation: (from data of conductometric method used for CMC measurement)

In aqueous solution and in salt solution the way of calculation of counter ion binding (β) is same.

$$\beta = (1 - \alpha)$$

$$\alpha = \frac{Slope\ of\ postmicellar\ zone}{Slope\ of\ premicellar\ zone}$$

Example: At 298K in aqueous TTAB solution

The value of post-micellar region = 25.38158 (by taking the Fit Linear)

The value of pre-micellar region = 89.96998 (by taking the Fit Linear)

Now, $\alpha = \frac{25.38158}{89.96998} = 0.2821$

So, $\beta = 0.7179$

Note: In all temperatures and in all medium α value was calculated in the same way.

Thermodynamic parameters calculation for aqueous TTAB solution

Mole fraction calculation:

At 298K, the CMC of aqueous TTAB solution = 3.75 mM. During this CMC value the total volume of the solution is (50+16.67) mL = 66.67 ml.

1000 ml 1M TTAB solution contains = 336.4 gm TTAB

So, 66.67 ml 0.00375 M SDS solution contains $= \frac{336.4 \times 66.67 \times 0.00375}{1000} = 0.0841$ gm TTAB

Mole of SDS $= \frac{0.0841}{336.4} = 2.5 \times 10^{-4}$

Mole of water $= \frac{66.67}{18} = 3.704$

Total mole $= 3.704 + 2.5 \times 10^{-4} = 3.704$

Mole fraction of TTAB at CMC$= (2.5 \times 10^{-4})/3.704 = 6.749 \times 10^{-5}$

At 298K, ln(CMC) = −9.604

Note: All the calculation for mole fraction has been calculated in the same way for TTAB in aqueous and in NaCl solution.

Free energy of micellization ($\Delta G_m{}^{\bullet}$):

At 298K, $(\Delta G_m{}^{\circ})_{298}$ = (1 + β) RT ln(CMC) = (1+0.7179)×8.314 ×298×(-9.604) = −40.877 kJmol^{-1}

Note: All the calculation for free energy of micellization ($\Delta G_m{}^{\circ}$) has been calculated in the same way for TTAB in aqueous and in NaCl solution.

Entropy Calculation ($\Delta S_m{}^{\bullet}$):

We know $(\Delta S_m{}^{\bullet}) = - \left\{ \dfrac{\partial(\Delta G_m^o)}{\partial T} \right\}_P$

Now, plotting the T vs. ($\Delta G_m{}^{\circ}$) graph for aqueous TTAB solution in excel sheet we get an equation like

$(\Delta G_m{}^{\circ})$ = 3.774 T^2−2310 T−31251

$\dfrac{\partial(\Delta G_m^{\circ})}{\partial T}$ = 2×3.774×T−2310

When T = 298K then $\dfrac{\partial(\Delta G_m^{\circ})}{\partial T}$ = −60.696

So for T = 298K

$(\Delta S_m{}^{\circ})$ = 60.696

Note: The same way has been followed for all calculations at different temperatures for TTAB in aqueous and in NaCl solution.

Enthalpy Calculation ($\Delta H_m{}^{0}$):

We know, $\Delta G_m{}^{\circ} = \Delta H_m{}^{\circ} - T\Delta S_m{}^{\circ}$

At 298K, $T\Delta S_m{}^{\circ}$= $\dfrac{298 \times 60.696}{1000}$ = 18.087 kJ/mol

So $\Delta H_m{}^{\circ} = -22.79$ kJ/mol

Note: In such a way we can calculate the value of $\Delta H_m{}^{\circ}$ for TTAB in aqueous and in NaCl solutions at different temperatures.

Thermodynamic parameters calculation for aqueous TTAB-0.0025 M NaCl solution at different temperatures

Mole fraction calculation:

At 298K, the CMC of TTAB solution = 3.34 mM. During this CMC value the total volume of the solution is (50+19.29) = 69.29 ml.

1000 ml 1 M TTAB solution contains = 336.4 gm TTAB

So, 69.29 ml 0.00334 M TTAB solution contains $= \frac{336.4 \times 69.29 \times 0.00334}{1000} = 0.0779$ gm TTAB

1000 ml 1 M NaCl solution contains 58.44 gm NaCl

So, 69.29 ml 0.0025 M NaCl solution contains 0.01 gm NaCl

Mole of TTAB $= \frac{0.0779}{336.4} = 2.316 \times 10^{-4}$

Mole of NaCl $= \frac{0.01}{58.44} = 1.711 \times 10^{-4}$

Mole of water $= \frac{69.29}{18} = 3.849$

Total mole $= 2.316 \times 10^{-4} + 1.711 \times 10^{-4} + 3.849 = 3.849$

Mole fraction of TTAB at CMC (X_{cmc}) $= 2.316 \times 10^{-4}/3.849 = 6.017 \times 10^{-5}$

Mole fraction of NaCl (X_s) $= 1.711 \times 10^{-5}/3.849 = 4.445 \times 10^{-5}$

Free energy calculation in presence of 0.005 M NaCl of SDS solution

$\Delta G_m° = RT [\ln X_{cmc} + (1-\alpha) \ln (X_{cmc} + X_s)]$

Here α = degree of dissociation

In the presence of 0.0025 M NaCl, the degree of dissociation of TTAB solution is found to be 0.2915

Now by putting the values from previous calculation we get

$\Delta G_m° = 8.314 \times 298 [(-9.718) + (1-0.2915) \times (-9.165)] = -40.165$ kJmol^{-1}K^{-1}

Note: We can calculate the value of $\Delta G_m°$ for TTAB at different temperatures in the same way.

Entropy calculation in the presence of 0.0025 M NaCl of TTAB solution

The way of calculation of entropy in presence of 0.0025 M NaCl follows the same way as for pure TTAB.

Enthalpy calculation in the presence of 0.005 M NaCl of TTAB solution

The way of calculation of enthalpy in presence of 0.0025 M NaCl follows the same way as for pure TTAB.

Adsorption

Thermodynamic parameters calculation for aqueous TTAB solution

Surface Excess Concentration: (from surface tension data)

$$\Gamma = -\frac{1}{2RT} \left(\frac{\partial \gamma}{\partial lnC}\right)_{T,P} = -\frac{1}{2.303 \times 2RT} \left(\frac{\partial \gamma}{\partial logC}\right)_{T,P}$$

In aqueous solution and in salt solution the way of calculation of Surface Excess Concentration Γ is same.

Example: At 298K in aqueous TTAB solution

Here the value of $\left(\frac{\partial \gamma}{\partial logC}\right) = -21.55114$ (from the slope of the surface tension data, calculated by Fit Linear)

$$\Gamma = -\frac{1 \times (-21.55114)}{2.303 \times 2 \times 8.314 \times 298 \times 1000} = 1.889 \times 10^{-6} \, \text{mol/m}^2$$

Note: In all temperatures and in all medium Γ value is calculated in the same way.

Equilibrium surface pressure:

$\pi_{cmc} = \gamma_o - \gamma_{cmc}$

At 298K for aqueous TTAB solution

$\gamma_o = 72.0$ mN/m, $\gamma_{cmc} = 36.4$ mN/m

So, $\pi_{cmc} = 35.6$ mN/m

Note: In all temperatures and in all medium π_{cmc} value is calculated in the same way.

Free energy of adsorption ($\Delta G_{ad}°$):

$(\Delta G_{ad}°) = (\Delta G_m°) - (\pi_{cmc} / \Gamma_{max})$

At 298K for aqueous TTAB solution

$(\Delta G_{ad}°) = (-40.877 - 18.846) = -59.723$ kJ/mol

Note: In all temperatures and in all medium ($\Delta G_{ad}°$) value is calculated in the same way.

Entropy calculation ($\Delta S_{ad}°$):

This calculation is done in the same way as micellization of TTAB in aqueous and in 0.0025 M NaCl solution.

Enthalpy calculation ($\Delta H_{ad}°$):

This calculation is done in the same way as micellization of TTAB in aqueous and in 0.0025 M NaCl solution.

Solubilization

Calculation of MSR at 298K for TTAB:

To get a calibration curve, at first, a fixed amount of dye was dissolved in a fixed amount of surfactant but several times higher concentration than CMC. The amount of dye to be like that it remains below to that of the solubilization equilibrium with surfactant micelle. Then carrying out
the UV-spectra, we get the following data-

Table: 1

Amount of dye (g)	Absorbance
0.00905	0.169
0.0181	0.316
0.0362	0.588
0.0724	1.137
0.0905	1.403
0.1086	1.695
0.11946	1.840
0.1448	2.237
0.1810	2.783
0.2172	3.299

Molar mass of sudan II is 276.33 g

276.33 g 1000 ml = 1 M

Therefore, 0.0025 g 25 ml = 3.62×10^{-4} M

By solubilizing dye (fixed amount) at different concentration (above and below CMC value) of TTAB we get the following data from UV-spectrophotogram

Table: 2

Surfactant concentration (mM)	Absorbance
1.5	0.028
2.0	0.033
2.5	0.061
3.0	0.075
3.5	0.323
4.0	0.682
4.5	0.992
5.5	1.648
6.0	2.038
6.5	2.421

Using absorbance data from Table-2, we can calculate corresponding concentration of dye that is absorbed from table 1 with the help of a plot.

Table: 3

Surfactant concentration (mM)	Dye concentration (mM)
1.5	5.56E-05
2.0	5.56E-05
2.5	0.00195
3.0	0.00283
3.5	0.01923
4.0	0.0429
4.5	0.06335
5.5	0.1067
6.0	0.1324
6.5	0.1576

PUBLICATIONS RELATED TO THE PRESENT WORK

1. Sharker, K.K.; Islam, M.N.; Das, S.; Counterion Effect on Krafft Temperature and Related Properties of Octadecyltrimethylammonium Bromide. *J. Surfact. Deterg.* (*in press*)
2. Das, S.; Islam, M.N.; Roy, J.C.; Influence of Electrolytes on the Physico-Chemical Properties of Tetradecyltrimethylammonium bromide in Aqueous Solution (to be submitted)