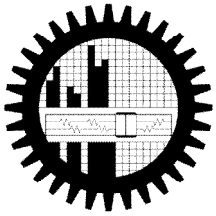
Adsorption and Micellar Behavior of Aqueous Ionic Surfactant Systems

By

Jagadish Chandra Roy

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF PHILOSOPHY (M.PHIL) IN CHEMISTRY



Department of Chemistry

Bangladesh University of Engineering and Technology

Dhaka-1000, Bangladesh

2013

Bangladesh University of Engineering and Technology, Dhaka

Department of Chemistry

Certification of Thesis

The thesis titled 'Adsorption and Micellar Behavior of Aqueous Ionic Surfactant Systems' is submitted by Jagadish Chandra Roy, Roll No: 0409033204F. Session: April 2009 has been accepted as satisfactory in partial fulfillment of the requirement for the degree of Master of Philosophy (M. Phil.) in Chemistry on April 28, 2013.

BOARD OF EXAMINERS

1. Dr. Md. Nazrul Islam
   Associate Professor
   Department of Chemistry
   BUET, Dhaka, Bangladesh
   (Supervisor)
   — Chairman

2. Dr. Shakila Rahman
   Head & Professor
   Department of Chemistry
   BUET, Dhaka, Bangladesh
   — Member (Ex-officio)

3. Dr. Md. Manwarul Islam
   Professor
   Department of Chemistry
   BUET, Dhaka, Bangladesh
   — Member

4. Dr. Al-Nakib Chowdhury
   Professor
   Department of Chemistry
   BUET, Dhaka, Bangladesh
   — Member

5. Dr. Mahbub Kabir
   Professor
   Department of Chemistry
   Jahangirnagar University,
   Savar, Bangladesh
   — Member (External)

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.

Signature of the Candidate

Jagadish Chandra Roy

Candidate

To our Freedom Fighters by whom our Motherland was born indebted to their Blood

Acknowledgement

I think the obvious first person to thank is Associate Professor Dr. Md. Nazrul Islam, without whom this entire project wouldn't exist, and so I would like to thank him for being my supervisor. On a more personal level, I am grateful for his ideas and patience, but most importantly his ability to teach and the enthusiasm he bestows upon others.

I would like to thank I also thank the members of the Board of Post-graduate Studies (BPGS) of the Department of Chemistry, BUET for helpful discussion during the preparation of the research project. The financial assistance (CASR-229/31) approved by the committee for Advanced Studies and Research (CASR), BUET for carrying out the present work is highly appreciated. Thank to Dr. Al-Nokib Chowdhury and His research group for their useful discussions and to Mr. Bin Yeamin, Mr. Arup for performing UV-vis spectroscopy and Centrifuge on my solubilization study of samples.

I would also like to thank Mr. Gazi Asrafuzzaman for their stimulating conversations in the classroom and over many points. Thanks to all the Stuffs of the Chemistry Department, Bangladesh University of Engineering and Technology (BUET): Mr. Mamun, Mr. Samsu, Mr. Belaet, Mr. Showkat. Whether it was through the power of positive thinking, encouragement, ability to listen, kindness, endless chemistry knowledge, or even flip cup abilities, you all played an important role in making my time here a positive experience.

The biggest of all of my acknowledgements goes to my parents for getting me here.

Jagadish Chandra Roy

Author

ABSTRACT

In the present work, the thermodynamic behavior of surface adsorption and micellization of cetyltrimethylammonium bromide (CTAB) and Tetradecyltrimethylammonium bromide (TTAB) in pure water and aqueous NaCl solution was investigated by surface tentiometric and conductometric methods. The CMC values of the surfactants in pure water gradually increased with increasing temperature. On the other hand, the CMC values of CTAB and TTAB in presence of NaCl increased and then decreased with increasing temperature and the values were found to be much lower than the corresponding values in pure water. Thus the CMC-Temperature data can be shown by a $\Lambda-$shaped curve. The micellar dissociation (fraction of counter-ion binding) and energetic parameters (free energy, enthalpy and entropy) of both adsorption and micellization were calculated. The processes were found to be both enthalpy and entropy controlled and appeared to be more and more enthalpy driven with an increase in temperature. An enthalpy-entropy compensation rule was found to hold for both adsorption and micellization processes. The krafft temperature (T_k) of the surfactant was found to decrease significantly with an increase in concentration of NaCl, which is a sharp contrast to the usual behavior of the effect of electrolytes on the T_k values of classical ionic surfactants. The surface excess concentration (Γ) of both surfactants in pure water was found to decrease gradually with increasing temperature. However, the values of Γ were much higher in the presence of NaCl compared to the corresponding values in pure water. The aggregation number (N_{agg}) of the surfactants in presence and in absence of NaCl has been measured. The aggregation numbers (N_{agg}) of the surfactants in the presence of NaCl were found to be higher than those in pure water. The solubilization behavior of a water-

insoluble dye, sudan red B (SRB) in the micellar system was studied by UV-visible spectrophotometric technique. The solubilization ratio in the presence of NaCl was found to be about three times higher than in pure water, indicating that the solubilization of SRB in the CTAB and TTAB micelles significantly increased with an increase in NaCl concentration.

Table of Contents

LIST OF FIGURES

LIST OF TABLES

1.1 BEHAVIOR OF SURFACTANTS IN AQUEOUS SOULTION

Surfactants are known to play a vital role in many processes of both fundamental and applied aspects[1]. They have a characteristic molecular structure consisting of a polar or changed head group that possesses strong affinity for water and a hydrophobic alkyl chain that does not. This unique duality towards an aqueous environment leads them to a wide variety of complex self-assembly in the bulk of aqueous solution. [1-9].On the other hand surfactant molecules dissolved in the bulk of the aqueous solution can form monolayers upon spontaneous adsorption at the air-water interface due to their preferential surface active nature. The spontaneous adsorption of surfactant molecules results in an increase the two-dimensional surface pressure with a consequent increase in surface density of the adsorbed molecules. If the delicate balance in the interactions between the hydrocarbon chains and polar head-groups permits, then at a definite temperature the two-dimensional adsorbed monolayer can undergo a pressure-induced phase transition showing a variety of patterns at the air-water interface[4]. However, high-density condensed-phase formation in adsorbed monolayers sometimes becomes difficult due to electrostatic repulsion, bulkiness as well as strong hydration of the polar head group. In such a case, hydrophobic interactions among the alkyl chains make it more favorable to remain in the bulk of the aqueous solution by forming micellar aggregates when the surfactant concentration attains a minimum value known as the critical micelle concentration (CMC). The CMC is a narrow concentration range over which surfactants show an abrupt change in a number of physical properties[1]. The occurrence of the CMC results from a delicate balance of thermodynamic forces between the favorable interaction between the hydrophobic alkyl chains and the opposing repulsive interaction between the head groups which depend on various factors such as temperature, dielectric constant of the medium, length of the alkyl

chain, presence of additives and relative size and charge of the headgroup.[7,8] The formation of micelles and its dependence on different factors such as temperature, additives, dielectric constant of the medium, the extent of counter-ion binding (for ionic surfactants), solubilization etc. are important physicochemical aspects that need detailed and intensive attention for both fundamental understanding and industrial applications. The dominance of the favorable interaction between alkyl chains of the surfactant favors micellization and lead CMC to lower values by stabilizing micelles while the opposing repulsive interaction between the polar/charged head groups disfavor micellization and leads CMC to higher values[7].Micelles are known to have an antisotropic water distribution within structure. In other words, the water concentration decreases from the bulk towards the interior of the micelle, with a completely hydrophobic-like interior. Thus, micellar solution consist of special medium in which hydrophobic organic compounds can be solubilized in aqueous surfactant solution, which are otherwise insoluble in water [10-17]. However, below the CMC surfactant molecule exist as monomers and have only little or no influence on the solubility of water-insoluble compounds. In other words, micellar solubilization occurs when the concentration is equal to or above the CMC value. Micelle-enhanced solubilization of nonpolar organic compounds is one of the most significant applications of surfactant. It provides the basis for detergency, micellar catalysis and extraction, and formation of microemulsion[15]. The extent of solubilization depends on many factors such as the structure of the surfactant, aggregation number, micellar geometry, and temperature, ionic strength of the medium and the nature of the solubilizate. The locus of solubilization of poorly water-soluble compounds in micellar systems depends on the polarity of solubilizate. Non-polar molecules are solubilized in the micelle core and substances with intermediate polarity are distributed along surfactant molecules in certain intermediate

position[15]. An increase in surfactant concentration in solution thus increases the extent of solubilization of hydrophobic solutes because of an increase in the number of micelles in the bulk. Studies of the solubilization of poorly water-soluble compounds in non-aqueous and aqueous system have revealed a lot of application in the practical fields such as drug carrier[10,13], drug solubilization[16], seperation[16], toxic waste removal[14,17] etc. The solubilizing capacity of a surfactant is usually expressed quantitatively by molar solubilization ratio (MSR). The MSR can be expressed as the number of moles of the substance solubilized per mole of the surfactant in solution[17]. The potential value of surfactant led to research on their use in drug delivery as drug carrier. Besides, surfactant micelles have been used as model systems for bio-membranes to study the interaction of different compounds including drug molecules with bio-membrane. A better understanding of interactions between surfactant allow for the more rational design and use of surfactants for biomedical application as well as understanding the biological system. Proper micelles, as defined above, do not occur in living systems to a great extent. The hydrophobic interaction, which is the main driving force for the formation of micelles from monomeric amphiphiles, is of fundamental importance for the spatial organization of chemical process in living systems. The basic building blocks of biological membranes are phospholipids. Due to the hydrophobic interaction, these amphiphiles spontaneously form lamellar structures when dispersed in water. Moreover, these extended lamellar structures can rather easily be disrupted so that a globular closed aggregate is formed, a so called vesicle, where only a single phospholipid bilayer can constitute a diaphragm between the outside and the inside water solutions. This might be the most spectacular example of the behavior of biological amphiphilic substances but the hydrophobic effect is of great importance in a number of other cases as for instance in determining protein conformation. A careful study of micellar

solutions is one way of attracting the general problem of the hydrophobic interaction. This for example, the point of view adopted by Tanford in his book "The hydrophobic effect"[18], where one can find a lot of additional cases where the hydrophobic interaction plays an important role in biological processes. In this short survey we will only point out some of the specific biological implications of the different aspects of micelle formation that will be presented in the upcoming sections. The general thermodynamic principles guiding the formation of micelles are equally valid for membrane formation or protein folding. There are good reasons to believe that the model expressions for the chemical potential developed by Tanford[19]. This model is valid also for phospholipid system. An interesting possibility would be to try describing phospholipid mixtures where phenomena like a lateral phase separation might occur. Much effort has been devoted to determining the physical state of the alkyl chains in the membrane bilayer. As for micelles, one normally finds a typical liquid like interior, which makes rapid molecular processes possible within the bilayer structure. However, with some phospholipids one can possibly have more solid-like structure under certain physiological conditions. It seems also settled that the interior of large globular proteins has some liquid-like properties and it is not as rigid as one might infer from the x-ray diffraction structure determinations. The process of solubilization is of tremendous importance for a number of physiological and pharmaceutical phenomena. It is well established that many types of membranes has a high content of solubilized cholesterol. The role of the cholesterol in the membranes is not clear. One relevant aspect of a nonpolar pharmaceutical substance is its non-specific ability to be solubilized in a membrane which is a complication that has to be considered when discussing physiological effects on the basis of studies on model systems. As for micelles, the hydrations of pure phospholipid bilayers do not seem to extend beyond the polar head-

groups. Consequently, such a bilayer constitutes an effective barrier for transport of polar substances in general and ions in particular. A transport through the bilayer can be made possibly by the use of a carrier or by the formation of a hydrophilic channel.It seems that ionic interactions are of considerable importance in controlling the functioning of biological membranes. For example, divalent cations as Mg^{2+} and Ca^{2+} have several important regulatory effects. Transport protein can bind electrostatically to the membrane surface which always contains some charged groups. It is clear that a study of ion binding properties of amphiphiles have important implications for these phenomena. The survey of biological implications of micelle formation is only to give some ideas to interpret studies regarding the present findings in wider range of area.

1.2 TYPES OF SURFACTANTS

Surfactants are amphiphilic compounds with well-segregated polar and a polar domains that have measurable aqueous solubility as both aggregates and as monomers. Surfactants belong to a class of compounds that reduce interfacial surface tension (in oil, water or both) by adsorbing to interfaces. The ability of a surfactant to participate in a specific biological/biochemical function is related to its structure; the polar hydrophilic portion of the surfactant molecule is referred to as the “hydrophilic head group” while the nonpolar hydrophobic, portion is referred to as the “tail” (Figure 2).The chemical composition of surfactants can vary greatly as alterations can be made to either the hydrophobic “tail” or hydrophilic “head” depending on the desired application. Surfactants are generally classified by the nature of their head group and the main classes include anionic, cationic, zwitterionic (amphoteric), non-ionic, and combinations of the above. A summary of the main classes, some examples, and their uses can be seen in Figure 1.4.

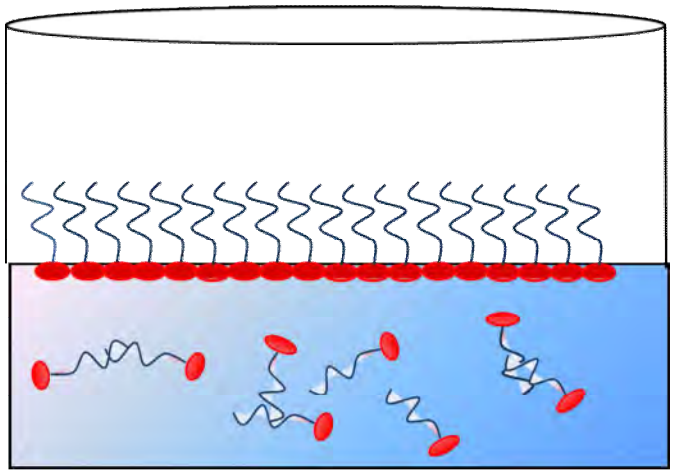
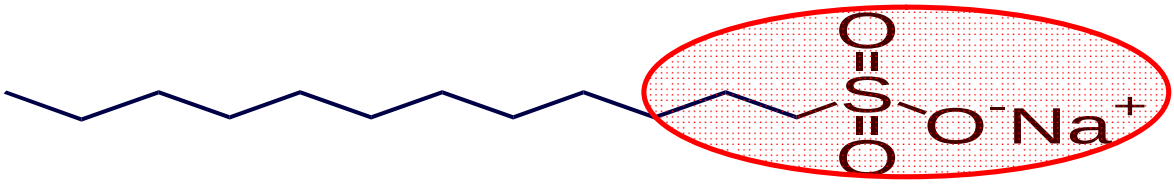


Figure1.1: Surfactants in the aqueous medium

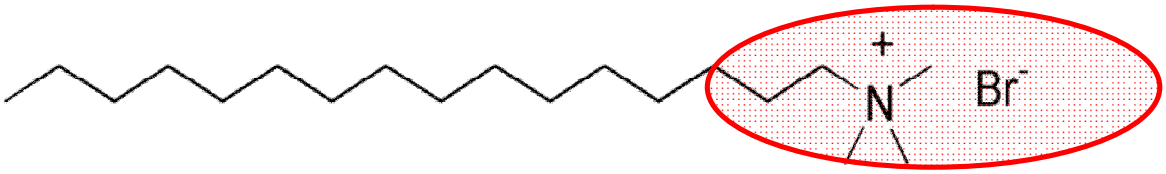
1.3 MICELLE

The solubility pattern with respect to solvent properties of a non-polar compound like alkane is in sharp contrast to that of a charged or otherwise strongly polar chemical species. If these two features occur simultaneously in the same chemical entity, interesting comprises are observed. For aqueous solutions, one well known situation is that the polar group is located in the solution while the nonpolar part seeks to avoid the aqueous environment by stretching into the gas phase or into an adjacent non-polar liquid phase. Except for this adsorption at gas –liquid, liquid-liquid or liquid-solid interfaces there is an alternative possibility to avoid the unfavorable contact between non-polar groups and water and between polar groups and non-polar solvent, i.e. by self-association into various type of aggregates. The term micelle is introduced by the pioneer in the field J.W McBain in 1913 to describe the formation of colloidal properties by detergents and soaps. The word "micelle" has also been used in biology and in colloid chemistry for other phenomena. Important features of the micelle are the high aggregation number and effective separation of hydrophilic and hydrophobic part. It was established at an early stage that micelle

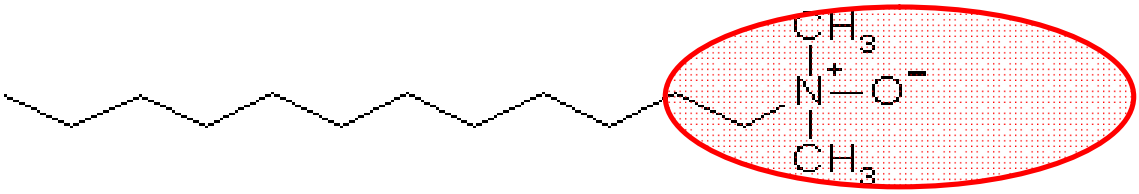
formation displays peculiar concentration dependence. Thus at low concentration an aqueous ionic surfactant solution behaves essentially as a strong electrolyte. On the other hand, an increased amphiphile concentration leads to a corresponding increase in the amount of micelles while the monomer concentration stays roughly independent of the total amphiphile concentration. The quite pronounced change in the concentration dependence of a large number of properties in the region where micelle formation starts and it is called critical micelle concentration (CMC). There are two common approaches to the theoretical treatment of amphiphile aggregation. In one, the so-called phase separation model, micelle formation is considered as analogous to a phase separation. The CMC is then the saturation concentration of the amphiphile in the monomeric state and micelles constitute the separated pseudo-phase. According to other approach, the equilibrium model, micelle formation is treated analogous to a chemical equilibrium. There is now general agreement that the equilibrium model provides a correct description of micelle formation. Analysis of the equilibria shows that for the cooperative formation of large aggregates, the onset of micelle formation effectively takes place in quite narrow concentration range. This observation makes the term CMC from a practical point of view since it gives an approximate figure well characterizing the self-association pattern of ascertain amphiphile. Although due caution must be exercised in making use of CMC data, their variation with various factor such as alkyl chain group, polar head-group, counter-ion, added electrolyte etc. needs considerable attention and has been most illuminating for acquiring of an understanding for several aspects of micelle formation.



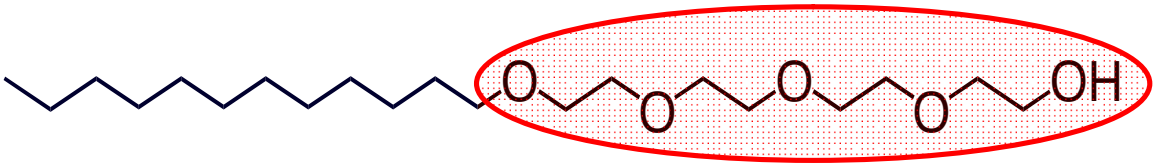
Sodium dodecylsulfate (SDS)
(Anionic)



C_{16}TABr – cetyltrimethylammonium bromide $C_{16}H_{33}N(CH_3)_3Br$
(cationic)



An amine oxide
(Zwitterionic)



Polyoxyethylene(4) lauryl ether (Brij 30)
(Nonionic)

Figure 1.2: Various types of surfactant and corresponding head-group (red color) and carbon tail(blue color)

1.4 THERMODYNAMICS OF MICELLE FORMATION

The occurrence of the CMC results from a delicate balance of intermolecular forces. The interplay among these forces is also responsible for the structural organization in living systems as for example, in bio-membranes. A thermodynamical description of micellar solutions has thus much wider implications than an understanding of the micellar system itself. As micelles are formed by readily available, easily purified and usually well-defined chemicals they are suitable model systems in experimental investigations of hydrophobic and hydrophilic effects. Different theoretical treatments can then be tested against experimental quantities like free energies of formation or CMC values, heat of formation, micellar size and shape and their variation with temperature. The effect of additives such as electrolyte or non-polar substances accounted for a theoretical description.The first attempt of a quantitative treatment of micellization was made by Debye[20,21]. Although quantitatively incorrect his work becomes a starting point but for refinement, four different approaches have been used in the thermodynamic description of surfactant aggregation. These are (pseudo) phase separation model, the mass action model, the small system model and the multiple equilibrium models. The two former approximations as such while the two latter can be used in a rigorous description.

1.4.1 Thermodynamic Models

1.4.1 (a) The phase separation model

A number of properties such as osmotic pressure, surface tension, equivalent conductivity show a change in concentration dependence around a particular concentration

called the critical micelle concentration. This behavior resembles very much what one finds for a transition into a two-phase region. This suggests that one might treat the micellar solution as a two phase system where the CMC is the concentration where the system enters the two- phase region. This is the so-called phase separation assumption. Although micellar systems are one-phase systems, the micellar association is cooperative to the extent that the phase separation model can be very useful. Through this approximation one renounces the possibility of describing properties of the micellar aggregates such as size and shape but the model is often important for the conceptual understanding of micellar systems. It is also very convenient in a quantitative analysis of the variation of molecular properties with concentration. When the micelles are regarded as a separate phase the chemical potential of the surfactant in the aqueous phase is

$$\mu_{aq} = \mu^{\theta}{}_{aq} + kTlnf_1X_1 \quad \text{.....(1.1)}$$

Where $\mu^{\theta}{}_{aq}$ expresses standard chemical potential, $f_1$denotes the activity coefficient and X_1 the monomer mole fraction. At a certain critical concentration $\chi^{cric}{}_1$the chemical potential in the aqueous phase equals that of micellar (pseudo) phase

$$\mu^{\theta}{}_{aq}\left(\chi^{cric}{}_1\right) = \mu^{\theta}{}_{mic} \quad \text{.....(1.2)}$$

and a phase separation occurs. The critical concentration then identified as the critical micelle concentration, X_{cric}=CMC. Below the CMC only monomers and possibly non-micellar aggregates exist, while above the CMC the concentration of non micellar molecules is constant. This result has important consequences. The mean value of any molecular property should vary linearly with concentration above the CMC and this should also be the case for the solubility of additive. These predictions are experimentally found to be only approximately correct. The discrepancies occur mainly for two reasons. At the CMC there is no true phase change and molecular properties change more gradually

without a discontinuity in the rate of change. Furthermore, the monomer activity does not stay quite constant above the CMC and this leads in some cases to important changes in micelle size and shape with concomitant change in molecular properties.

1.4.1 (b) The mass action model

In the case of ionic surfactants the equilibrium model is preferable because it is possible to take in consideration, in an explicit way, the effect of the counter-ion dissociation. The equilibrium model considers that the micellization process can be described by equilibrium between monomers, counter-ions, and mono-disperse micelles. In the case of a cationic surfactant this equilibrium can be represented by

$$nS^+ + (n-p)C^- \rightleftarrows M^{p+} \quad \text{.....(1.3)}$$

where S^+ represents the surfactant cations, C^- the corresponding counter-ions, 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^o_{mic}, is given by

$$\Delta G^o_{mic} = RT\left(-\frac{1}{n} ln a_{M^{p+}} + ln a_{S^+} + \left(1-\frac{p}{n}\right) ln a_{C^-}\right) \quad \text{.....(1.4)}$$

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

$$\Delta G^o_{mic} = (2-\beta) RT ln X_{CMC} \quad \text{.....(1.5)}$$

Where β ($\beta = p/n$) is the degree of counter-ion dissociation. If the change in $\beta$with temperature is small, as occurs in our case over the temperature range studied, enthalpy yields

$$\Delta H_{mic}^{o} = -(2-\beta)RT^{2}\,(\frac{\partial ln X_{CMC}}{\partial T})_{p} \quad \text{.....(1.6)}$$

In this way, the enthalpy of micellization can be evaluated from the slope of a tangent to a plot of $ln(X_{\mathrm{CMC}})$ versus T at a particular temperature. In all the cases the best fit can be found to be a second-order polynomial. In addition, once ΔG_{mic}^{o} and ΔH_{mic}^{o} have been obtained, the entropy of micellization can be estimated from

$$\Delta H_{m}^{o} = T\Delta S_{m}^{o} + \Delta G_{m}^{o} \quad \text{.....(1.7)}$$

In the mass action model one has a description of the system through only one parameter and yet a smooth transition in the CMC region.

1.4.1(c) The multiple equilibrium models

The obvious extension of the mass action model is to introduce aggregates of different sizes which are in equilibrium with each other. These multiple equilibria can be formally written in two equivalent ways. Either one has a stepwise growth of the micelle according to the scheme

$M_1 + M_{n-1} \rightleftarrows M_n$ n=2, 3……..……..……(1.8)

Or one can regard each aggregate to be formed directly from the monomers

$nM_1 \rightleftarrows M_n$, n=2,3……(1.9)

For the first equation the equilibrium constant is

$K_n = (f_n X_n / n) / \{f_1 X_1 . (f_{n-1} X_{n-1}) / (n-1)\}$…….(1.10)

And the aggregation process is determined through the values of the constants K_n. An alternative formulation is obtained by writing the chemical potential μ_n of the aggregate M_n as

$$\mu_n = n\mu_n^{\theta} + \mathrm{kT}(f_n X_n / n) \quad \text{.....(1.11)}$$

Where μ_n^{θ} is the standard chemical potential per monomer in the micelle. The chemical potentials of the monomer in the micelle and in the aqueous solution are equal at equilibrium and from eq^n(1.1) and (1.11) for all n

$$\mu_n^{\theta} + \frac{kT}{n} ln(f_n X_n / n) = \mu^{\theta}{}_{aq} + kT ln f_1 X_1 \quad \text{.....(1.12)}$$

The mole fraction of aggregation n is

$$\frac{X_n}{n} = \left\{ f_1 X_1 \, exp\left[(\mu_{aq}^{\theta} - \mu_n^{\theta}) / kT \right] \right\}^n / f_n \quad \text{.....(1.13)}$$

Together with the expression for the total concentration S of surfactant molecules

$$S = \sum_i X_i \quad \text{.....(1.14)}$$

Equation (1.13) determines the size distribution in the micellar solution. The eqns. (1.10) and (1.12) are related through

$$-kT \sum_{i=2}^{n} \ln K_i = n\left(\mu_n^{\theta} - \mu_{aq}^{\theta}\right) \quad \text{.....(1.15)}$$

Depending on the actual application either eq. (1.10) or (1.12) is the most convenient one to use in a description of surfactant aggregation to micelles. No distinction between ionic and non-ionic amphiphiles has been made by this model. For the ionic amphiphiles it is possible to include the counter-ions explicitly in the chemical equilibria. The number of chemical species is then greatly enhanced, which makes the approach less useful. Instead the counter-ions are usually regarded as members of the ion cloud surrounding the charged micelle. Changes in ion binding have then to be accounted for through changes in the activity coefficients or in the standard chemical potentials.

1.5 MICELLE AS A MICRO-SYSTEM

When one wants to account for the concentration dependence of micellar properties the phase separation or mass action model are usually sufficiently accurate, but as soon as changes in micelle size and shape have to be accounted for one must introduce refinements in the models. The phase separation model can be extended into a formally rigorous framework. The method was developed by Hill[22]and called thermodynamics of small systems. In this approach, the micelle is regarded as surrounded by a bath which defines the so called environmental variables. Hill showed that the maximum number of independent intensive variables is more for the small system than for a corresponding macroscopic system. Micelles of different size are in dynamic equilibrium with each other and for such a case the relevant intensive environmental variables are the temperature, T, the pressure, P and the chemical potential of the monomers in the aqueous solutionm_{aq}. These intensive variables determine properties like micelle size distribution. However, the work by Hall has not been followed up by other workers in the field and it seems that the small system thermodynamics involves an unnecessarily complicated formalism for most applications.[23]

1.6 LITERATURE SURVEY (FACTORS RESPONSIBLE FOR MICELLE SELF-AGGREGATION

1.6.1 Hydrophobic Interaction

One of the important features that make water unique as a solvent is its response to a-polar solutes. These have low solubility in water. These have low solubility is caused

mainly by entropy effects[24]. This suggests that the cause of interaction between a-polar molecules and solvent water is to be found in peculiarities in the structure of liquid water. The tendency for a-polar molecules or molecular fragments to avoid contact with water is said to be due to the hydrophobic interaction, which thus gives rise to a thermodynamic force rather than a mechanical force. The hydrophobic interaction has been extensively studied and for recent survey of the subject one can consult a review by Franks[24].The mechanism of surfactant self-assembly has been studied extensively. However, it is still unclear. From a thermodynamic point of view, surfactant self-assembly is entropy driven process. When temperature is increased, entropy of water is increased due to the destruction of structured water around the hydrophobic tail and entropy of surfactant is decreased a little compared to the water. Even though it is an endothermic process, the free energy of the whole process is negative which suggests micelle formation is a spontaneous process. Generally, the water molecules are arranged in an ordered way around the monomeric units of micelles, which can be defined as 'iceberg'. During micellization, due to the destruction of the iceberg a positive entropy change occurs. Despite this micellization-favoring phenomenon, a negative change can occur if the ordering of the randomly oriented amphiphile molecules from the solvated form into a micelle structure is more pronounced than disordering effect due to the destruction of icebergs around the alkyl chains. At the same time, the motion of the water molecules bound to the hydrophilic heads become more restricted, contributing to the decrease in entropy.

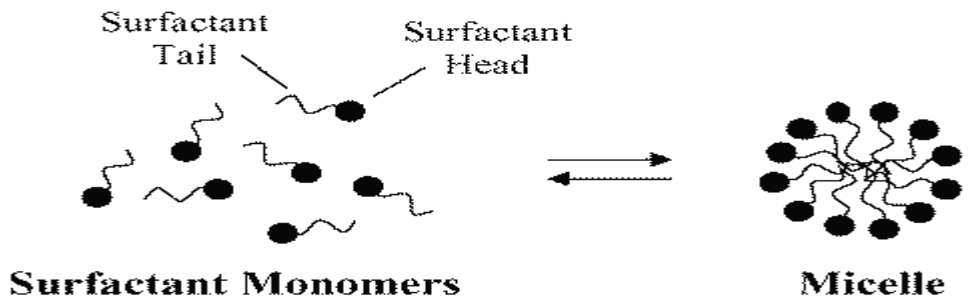


Figure 1.3: Micelle formation from monomeric surfactants

1.6.2 Hydration

Water has several peculiar properties like a density increase on melting and a high boiling point and these are now rather well understood on a molecular basis. In liquid water, the fraction of broken hydrogen-bond is rather small and the water-water distances are only slightly longer than that in ice. The coordination number is slightly larger than four and the coordination is approximately tetrahedral. The structure of liquid is a very open one and according to the X-ray scattering studies[25] it is closely similar to that of ice but with some non-hydrogen bonded water molecules in interstitial positions. Due to its highly structured nature, water as a solvent displays a very complex behavior. Thus in addition to direct ion-molecule interactions also the effect of a solute on the hydrogen bonded network is of paramount importance. In the present context it is most significant to note that non-polar solutes have particularly great influences on water structure. Thus alkyl groups markedly reduce both the rotational and the translational mobility of the water molecules[26] and marked "Structure-stabilizing" effect is evident also from a large decrease in partial molal entropy and an increase in partial molal heat capacity on introduction of alkyl containing solutes[24]. The entropically unfavorable solution of nonpolar molecules or

group in water has been termed “hydrophobic hydration” to distinguish it from enthalpy-driven process due to ion-dipole interactions and hydrogen-bonding. (Hydrophobic interaction leading to a gain in entropy is the partial reversal of the hydrophobic hydration) The exact structural nature of the hydrophobic hydration is known but a location of the solute in “holes” in the open solvent structure in an often discussed idea which is supported by negative excess partial molar volumes(-15 cm^3 per mole of CH2 groups) [24]. Crystalline hydrates[27] of many non-polar compounds show a striking stability even for high hydration numbers, X-ray diffraction studies have established their structure to be of the clathrate type, with the solute surrounded by a layer of hydrogen-bonded water molecules forming, for example, pentagonal dodecahedra. Thus even if the detailed structure is not presently established, it can be assumed that alkyl chain of an amphipile monomer in water is surrounded by a hydrogen-bonded organized water layer. Except for thermodynamic observation[24], this is supported by observations of large effects of surfactant molecules on the molecular motion of water (rotational and translational) below the CMC[28,29]. The polar heads of the monomer interact with water in away similar to simple polar solutes and electrolytes through hydrogen-bond, dipole-dipole and ion-dipole interactions. It is evident that these hydration features are affected when the amphiphile enters a micelle but the question of the extent and nature of the changes has been given rise to considerable controversy in recent year. It is clear that an understanding of micellization must involve a detailed geometrical description of the hydration of the different parts of the micelle, but it will be seen that merely a global hydration number can be quite informative in eliminating certain of the hypotheses advanced. The concept of a single hydration number to describe the solute-water interaction is of course a simplification and it is well known that the definition of the hydration number is dependent on the experimental approach[30]. A suitable

definition for the present purpose is to take the micelle hydration water number as the number of water molecules moving with the micelle as a kinetic entity in solution. Then the hydration number can be determined from the transport properties, e.g. viscosity data is given by Mukherjee[31]. The procedure involves determination of the intrinsic viscosity and comparing it with the partial specific volume of the amphiphile. The micelle hydration numbers per amphiphile obtained by Mukharjee were 9 for SDS and hydration number 5 for CTAC and TTAC. A similar procedure was used by Ekwall and Holmberg[32] to obtain a hydration number of 8.5-8.9 for sodium octanoate micelles and by Courchene[33] to obtain hydration number 10 for dimethyldodecylamineoxide micelles. Tokiwa and Ohki[34] used viscosity data as well as combined sedimentation and diffusion data to obtain micellar hydration numbers. For SDS, hydration number 8 was combined while for a series of sodium dodecylpolyoxyethylene sulfates, the hydration number increases strongly with the number of oxyethylene units. The study of the water self-diffusion coefficient as a function of micellar concentration is another efficient way of obtaining hydration number and in this way the hydration number was determined to be 8.7 for sodium octanoate micelles[29]. The hydration numbers given are somewhat approximate and are affected by sources of error in the evaluation but it seems that any correction should lower these numbers which can therefore serve as rather reliable upper limits. As noted by Mukherjee[31] these values are smaller than those estimated for a uniform monolayer of water at the micellar surface. Mukherjee also observed that the hydration numbers can be approximately understood in terms of hydration of the bound counter-ions and the polar heads alone. Water contact of the alkyl chain is not suggested by these data. On the other hand, partial molar volume data were taken to imply that also the α-CH_2 group adjacent to the polar head is in contact with water[39] but this interpretation has been criticized[36]. Hydration of non-ionic surfactants has

been studied to a small extent; one reason is that difficulty in studies hydrodynamic parameter for systems where micellar size and shape are so sensitive to temperature and concentration effects. Important contributions are due to Elworthyet al[37-39] who performed viscosity and water vapor pressure studies of solutions of the compound. Hydration was found, firstly according to expectation to increase with the number of oxyethylene groups and secondly, in contrast to what is often stated in the literature, with the temperature. However, in regard to the latter point information is rather sparse. For lamellar liquid crystals of water and $CH_3(CH_2)_8C_6H_4(OCH_2CH_2)_xOH$ (x=6 or 10) the observation of deuteron quadruple splitting which change only little with temperature[40] suggests an increased hydration with increasing temperature since the order parameter is expected to decrease markedly. For lecithin mesophase a marked increase in hydration with increasing temperature has been observed[41].There are also various spectroscopic methods for the study of amphiphile hydration. Deuteron quadruple splitting studies may provide information on the number of water molecules influenced in their orientation by the amphiphile aggregates in liquid crystals. For the lamellar phase of the systems alkali octanoate-decanol-water, for example, at most about 5 water molecules per octanate are appreciably oriented[42]. The order parameter of hydration water indicates a high mobility; correspondingly the water molecules at the surface of a micelle are certainly quite mobile. Proton NMR chemical shifts and relocation rates of water in sodium alkyl sulfate solutions change at a lower rate after the CMC than before demonstrating the decreased hydration[43,28]; however, conclusion are difficult to make. Various spectroscopic method, and in particular magnetic resonance techniques, should in principle be helpful in this respect but hitherto few adequate studies have been presented. Proton NMR of the alkyl chain suffers very much from the low resolution and the small chemical shift range but a

study at 220 MHz of proton chemical shifts and relaxation times by Podo[44] on some non-ionic polyoxyethylene containing compounds was informative. Thus the alkyl groups were found not to be in study by Clemett[45] of *n*-decylpentaoxyethyleneglycol mono-ether led to the same conclusion while proton chemical shifts were interpreted differently[46]. Concluding our discussion on the hydration of micellized amphipile and the degree of water penetration we may state that the polar head-groups certainly are hydrated although to a varying extent and there seems to be no evidence for any water inside the micelle core formed by the alkyl chains. It is safe to assume that there is only a small water penetration beyond the α-CH_2 group and there is furthermore, no good experimental demonstration of a marked contact between these groups and there is furthermore, no good experimental demonstration of a marked contact between this group and water. Even if the α-CH_2 water contact thus seems to be small some must probably occurs solely for geometrical reasons. Turning away from the micellar field it is easy to find strong support for the adopted view of a negligible alkyl chain-water contact besides the low solubility of water in hydrocarbon. Thus very low water content in the non-polar region is demonstrated by the slow passage of water through lipid bilayers[47] or between reversed micelles[48].

1.6.3 Counter-ion Binding

Although the formation of micelles from ionic and nonionic surfactants is qualitatively similar, there are important quantities differences. For nonionic amphiphiles the micelles form at much lower concentrations and hence a larger tendency to aggregate compared to ionic ones. The size of ionic amphiphile micelles increases on addition of electrolyte and if affected, decreases on increasing temperature. For non-ionics, on the

other hand, the micelle size relatively unaffected by added electrolytes. These differences are basically due to the importance of electrostatic interactions, for which a quite detailed picture of counter-ion binding is required. We can estimate the gross number of counter-ion binding to the micelle, so we also need information on geometric features of the counter-ion binding, on modes of interaction, and ion specificity effects, on counter-ion hydration etc. In the case of counter-ion binding to micelles, there is unambiguous distinction between bound and free counter-ions. Instead, the counter-ion concentration as a function of the distance from the micelles show a gradual decrease in going outwards with no well-defined transition point. There are a large number of experimental methods which are useful for studying counter-ion binding to micelles such as freezing point depression, vapor pressure lowering, and change of CMC with salt addition, electrical conductance, ion activity measurements, light scattering and self-diffusion[49,50] . Different methods may make quite different distinctions between free and bound counter-ions and it is of no surprise, therefore, that data on counter-ion binding from different types of studies may be very different. This is especially well exemplified in the study of Mukharjee[51]. On the other hand, trends in counter-ion binding with ionic radius are faithfully reproduced by most experimental approaches. It appears that methods where one monitors directly the counter-ion itself should be advantageous and one such method which has been found to work well is based on the translational self-diffusion coefficient of the counter-ion[29]. Comparing this with the micellar self-diffusion co-efficient gives the degree of counter-ion association, provided the self-diffusion coefficient of the ions not bound is known. The value so obtained corresponds to the number of counter-ions moving with the micelle as a kinetic entity. Such a definition has been found to be most useful in the theoretical treatment of counter-ion binding to micelles. Among the results obtained, it can be

mentioned that α close to 0.6 for sodium ion binding to a number of anionic surfactant micelles. For CTAB, α is 0.7 and both in this case and in the case of sodium octanate, a slight increase in α with increase concentration was noted. Except for this, the invariance of α is notable and the similarity of α for different cases is also evident from other types of studies.Mukharjee[51] has inferred slightly larger degree of dissociation of Li^+ than of Na^+ from dodecylsulfate micelles but otherwise there is little information available on ion specific effects on the micellar charge. It has been reported[51]that the CMC of alkali dodecylsulfates increases with decreasing atomic number showing that the counter-ion interaction follows the effective radius of the hydrated ion. For tetraalkylammonium counter-ions, CMC decreases with increasing ion size and this was attributed to a balancing of hydrophobic and electrostatic interactions. For the carboxylate end group there is no systematic study available on the variation of CMC with counter-ion. In general, counter-ion specificity is more pronounced in the case of cationic surfactants than in the case of anionic ones, and this can certainly to a great extent to be explained by a weaker hydration of typical counter anions. CMC of *n*-dodecyltrimethylammonium salts follows the sequence $NO_3^-<Br^-<Cl^-$ and this sequence persists in the presence of added sodium salt of the anion[52]. Likewise the CMC of CTAB is considerably lower than of the corresponding chloride (CTAC).By using ion-specific electrodes, Larson and Magid[53]showed NO_3^- to displace Br^- from the micelles in CTAB solution. A peculiar difference between micelles of CTAB and CTAC is that at room temperature a pronounced transition to very long micelles takes place in the former case while the micelles remain approximately spherical up to the highest concentration in the latter case[54,55]. Similarly, a marked viscoelastic behavior can occur for the same amphiphile with certain anions already at low concentration but has been observed over a wide concentration range for

others[56]. In solution containing both CTAB and CTAC, where spherical and long rod-like micelles seem to co-exist, Br^- ions show preferential binding to rod-like micelles and Cl^- to spherical ones[57]. For cationic amphiphiles, counter-ion specificity is also indicated in phase diagram[58] but systematic studies of the counter-ion dependence have not yet been reported. Because of the possibility of charge transfer, interactions between polar head and halide ions, ion specific interactions can be expected. In addition, CMC varies appreciably with counter-ion by the following order $I^-<Br^-<Cl^-$[59] and the same sequence applies to counter-ion dissociation[60]. Charge transfer complexes of dodecylpyridium iodide micelles were examined spectroscopically by Mukharjee and Ray[60-62] who also discussed in detail the specificity of the counter-ion adsorption. The size of hexadecylpyridium micelles is very sensitive to the anion of added salt, aggregation being promoted according to the sequence $F^-<Cl^-<Br^-<NO_3^-<I^-$[63]. Decreasing CMC with increasing counter-ion size for dodecylsulfate[51] and tetradecylpyridium salts as well as an increased surfactant ion residence time in the micelle[64] are two types of the observation pointing to a micelle stabilizing effect due to surfactant counter-ion and hydrophobic interactions. Fundamental to our picture of counter-ion binding to micelles is the knowledge of whether counter-ions retain their hydration sheaths or not on binding. Mukharjee[65] concluded from partial molar volume data that it is the interaction of the hydrated alkali ion with the micelle retains low water contents in surfactant system. An early ^{23}Na NMR relaxation study[66] indicated that the Na^+ ion retains its inner hydration layer down to quite low water contents in surfactant systems. Also the marked counter-ion specificity observed in certain cases is difficult to understand if the counter-ion retained completely their hydration layer. It is thus possible that at least Br^- and I^- ions become partially dehydrated when bound to micelles but there exists certainly no conclusive evidence. Stigter[67]and Mukharjee[68]considered that Cl^- anion

retains its hydration water on binding to micelles. To find out a theoretical description of ionic interaction in micellar solution, the contributions of Stigter[67,69,70] are most important. A natural starting point is to make use of electrical double layer theory approximating the micelle as a uniformly charged sphere with the counter-ion forming a surrounding Gouy-Chapman diffuse double layer. The distribution of counter-ions and the values of thermodynamic quantities can then be deduced by using the Poisson-Boltzmann equation. To eliminate the Gouy-Chapman approach, Stigter[67] introduced a more detailed model involving a stern layer inside the shear surface in addition to a diffuse Gouy-Chapman approach; Stigter[67]introduced a more detailed model involving a stern layer inside the shear surface in addition to a diffuse Gouy-Chapman layer outside the shear surface. For the stern layer, the discrete nature and size of the counter-ion and of the ionic head-groups are taken into account, and furthermore, the possibility of specific counter-ion adsorption is introduced. In treating the specific adsorption energy, account was taken for "image forces" resulting when the counter-ion approaches the micellar core with its low dielectric constant[67]. Image forces can also well rationalize the variation of CMC with charge distribution of the polar head in decyloyridium bromides[71]. Stigter[69,70] has developed a more detailed model of the stern layer and discussed the distribution therein of head-groups and counter-ions using lattice and cell theories of two component system. Although the theoretical work has added much to our knowledge of electrostatic effect of micellar systems, the limitations stand out clearly; deficiencies concern, for example, the discontinuity in the ion distribution between the stern and Gouy-Chapman layers and the use of macroscopic dielectric constants. As a general conclusion it may perhaps be said that the gross features of the counter-ion distribution between the kinetic micelle and the bulk solution can be understood in simplified electrostatic models, while the variation of it

with the system characteristics, the exact location of counter-ions and head-groups in the Stern layer etc. require sophisticated treatments. A striking observation is that the counter-ion association is roughly constant when such features as surfactant concentration, electrolyte addition, solubilization, phase structure and head group structure are varied. Similar observations apply for polyelectrolyte systems, where the phenomena is termed counter-ion condensation, implying that the net charge density of poly-electrolytes is neutralized by counter-ion binding to essentially the same constant value irrespective of other system parameters[72]. The counter-ion condensation for linear poly-ions has got a theoretical basis in solutions of the Poisson-Boltzmann equation for point charges in the presence of a continuous line charge of high charge density making two-phase approximation[72]. It seems most probable that a consideration of the counter-ion condensation model should be profitable not only for rod-like micelle but also for spherical ones as well as for lamellar meso-phase.

1.6.4 Krafft Point for Ionic Surfactants

The solubility of a surfactant is not linearly related to solvent temperature, but rather a temperature exists at which there is a sharp increase in the solubility of a surfactant. At this temperature, the concentration of the surfactant becomes equal to the CMC and is defined as the Krafft temperature or point (T_k), which varies for each surfactant. Most surfactants are used above this temperature to ensure the maximum surface tension reduction by overcoming the CMC. So, increase of the krafft point in presence of electrolyte solution of cationic surfactant (For example, CTAB) which bears same anioic part (For example, NaBr) or electrolyte (For example, NaCl) with Hexapyridinium Chloride (CPC)[73,74]was reported by some investigators. The increase of

the Krafft point is not suitable for industrial use. Since in application, surfactant generally use above the krafft point, the decrease of krafft point in the study of surfactant bears great importance but the related work is very few in number.

1.7 APPLICATION OF SURFACTANTS

Surfactant and its application: Surfactants are used in numerous applications including:

1.7.1 Detergents and Cleaners

The primary traditional application for surfactants is their use as soaps and detergents for a wide variety of cleaning processes. Soap has been used in personal hygiene for well over 2000 years with little change in the basic chemistry of their production and use. New products with pleasant colors, odors, and deodorant and antiperspirant activity have creptin to the market since the early twentieth century. On the other hand, the synthetic detergents used in cleaning our clothes, dishes, houses, and so on are relative newcomers. ‘‘Whiter than white’’ and ‘‘squeaky clean’’ commercials notwithstanding, the purpose of detergents is to remove unwanted dirt, oils, and other pollutants, while not doing irreparable damage to the substrate. In the past, due primarily to the shortcomings of available surfactants, such cleaning usually involved energy-intensive treatments very hot water and significant mechanical agitation. Modern surfactant and detergent formulations have made it possible for us to attain the same or better results with much lower wash temperatures and less mechanical energy consumption. Improved surfactants and detergent formulations have also resulted in less water use and more

Table 1.1 Summary of main classes of surfactants.

Class	Head Group	Applications
Anionic	$-CO_2^- Na^+$	Soaps
	$-SO_3^-Na+$	Synthetic detergents
	$-O-SO_3^- Na+$	Detergents, personal care products
	$-O-PO_3^-Na+$	Corrosion inhibitors, emulsifiers
	$-(OCH2CH2)n-O-SO_3^- Na+$	Liquid detergents, toiletries, emulsifiers
Cationic	$-N(CH3)3^+ Br^-$	Bitumen emulsions
	$>N(CH3)2^+ Br^-$	Bactericides, antistatic agents
		Fabric and hair conditioners
Zwitterionic	$-N^+(CH3)2-CH2-CO2^-$	Shampoos, cosmetics
	$-N^+(CH3)-CH2-SO3^-$	
Non-ionic	$-(OCH2CH2)nOH$	Detergents, emulsifiers

efficient biological degradation processes that help protect our environment. Even with lower wash temperatures and lower energy consumption, extensive studies have shown that equivalent or improved hygiene is maintained. It is only in instances where particularly dangerous pathogenic agents are present, as in hospital laundries, for example, that additional germicidal additives become necessary to obtain efficient cleaning results.

1.7.2. Cosmetics and Personal Care Products

Cosmetics and personal care products make up a vast multi-billion-dollar market worldwide, a market that continues to grow as a result of improved overall living standards in areas such as Asia and Latin America and continuing cultural driving forces in the already developed economies. Traditionally, such products have been made primarily from fats and oils, which often are perceived to have the advantage of occurring naturally in the human body and therefore present fewer problems in terms of toxicity, allergenicity, and so on. The perception is, of course, totally false, as shown by the large number of quite nasty allergens and toxins that come from the most ‘‘natural’’ of sources. Nonetheless, natural surfactants and other amphiphilic materials have been used in cosmetics since their ‘‘invention’’ in ancient Egypt (or before). It is probably safe to say that few, if any, cosmetic products known to women (or men, for that matter) are formulated without at least a small amount of a surfactant or surface-active component. That includes not only the more or less obvious creams and emulsions but also such decorative products as lipstick; rouge; mascara; and hair dyes, tints, and rinses. An important aspect of such products is, of course, the interaction of the components of the cosmetic formulation with the human skin, membranes, and other tissues or organs with which it will come into contact during use. As mentioned above, merely because a product is ‘‘natural’’ or is derived from a natural source does not guarantee that it will not produce an adverse reaction in some, if not all, users. The possible adverse effects of surfactants in cosmetics and personal care products must, of course, be studied in depth for obvious safety reasons as well as for questions of corporate liability and image. Unfortunately, our understanding of the chemical reactions or interactions among surfactants, biological membranes, and other components and structures is not sufficiently advanced to allow the formulator to say

with sufficient certainty what reaction an individual will have when in contact with a surfactant.

1.7.3. Textiles and Fibers

Surfactants have historically played an important role in the textile and fibers industry. The dyeing of textiles is an obvious application of surfactants. The added surfactants serve to aid in the uniform dispersion of the dyes in the dying solution, the penetration of the dying solution into the fiber matrix, the proper deposition of the dyes on the fiber surface, and the proper ‘‘fixing’’ of the dye to that surface. For natural fibers, the role of surfactants begins at the beginning with the washing and preparation of the crude fiber in preparation for spinning. Once the crude material is ready for spinning, the use of surfactants as internal lubricants and static discharge agents allows the industry to produce yarns in extremely long and fine filaments that would be impossible to handle otherwise. Extremely fast modern spinning and weaving equipment requires that the fibers pass through the process without breaking or jamming, events that would produce very expensive production line stoppages. Sewing equipment that may work at more than 6000stitches per minute requires that the fibers and needles pass in the night with a minimum of friction that could produce a significant amount of frictional heat and even burn the fibers. That interaction is controlled by the use of the proper surfactant. Synthetic fibers also require surfactants at various steps in their evolution from monomeric organic chemicals to finished cloth. Depending on the type of polymer involved, the process may require surfactants beginning with the polymer synthesis, but certainly once the first extrusion and spinning processes begin. Even after the textile is ‘‘finished’’ it is common to apply a final treatment with a surface-active material to define the final characteristics of

the product. In woven polyester rugs, for example, a final finish with an antistatic surfactant reduces or eliminates problems with static discharge (those shocking doorknobs in winter) and retards the adhesion of dirt to the fibers. The applications of fluorinated materials produces the stain repelling ‘‘Scotch Guard’’ effect by coating the fibers with a Teflon like armor.

1.7.4. Leather and Furs

Surfactants are an important part of the manufacture of leather and furs, starting with the original untreated skin or hide and ending with the finished product. In leather tanning, for example, it is normal to treat the leather 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. Similar applications are found in the fur industry.

1.7.5 Paints, Lacquers, and Other Coating Products

It is probably not surprising to find that surfactants are required in many capacities

in the production of paints and lacquers, and in related coating systems. In all paints that carry pigment loads, it is necessary to prepare a uniform dispersion that has reasonable stability to flocculation and coalescence. In addition, the preparation of mineral pigments involves the process of grinding the solid material down to the desired particle size, which is an energy-intensive process. In general, it is found that a smaller, more uniform particle size results in a higher covering power for the same weight load of pigment, that is, a more efficient use of material and consequently a reduction in cost always a nice effect in commerce. The grinding process is helped by reducing the surface energy of the solid pigment, an effect achieved by the addition of surfactants. Since pigment solids are far from smooth surfaces at the molecular level, the raw material will have small cracks and holes that serve as initiation points for the rupture of the structure. In the presence of the proper surfactant, the molecules penetrate into the cracks and crevices, adsorb onto the solid surface, and significantly reduce the surface energy of newly exposed solid, facilitating the continued breaking of the large particles into smaller units. The adsorbed surfactant molecules also create a barrier like coating that helps prevent the small particles from adhering or agglomerating. It is estimated that the use of surfactants in the grinding process can save up to 75% of the energy needed to achieve the same result without added surfactant. Once the pigment is properly ground, it must be mixed into the basic liquid carrier and maintained stable or easily dispersible for an extended period of time, much against the natural driving force of thermodynamics. For the dispersion of the pigment in the final coating formulation, it may be necessary to add additional surfactant of the same or another class. In organic coating systems, the surfactant may in fact be a polymeric system that doubles as the final dried binder for the pigment. On the other hand, there is available low-molecular-weight surfactants specifically designed to act in organic solvents.

In aqueous or latex paints, the surfactant is important not only in the pigment grinding process but also in the preparation of the latex polymer itself. The chemistry of emulsion polymerization (i.e., latex formation) is a complex and interesting phenomenon and cannot be treated here. Very few emulsion polymers are produced without the addition of surfactants, and most of those so prepared are interesting laboratory novelties that never see the light of commercial exposure. In addition to surfactants for pigment grinding and dispersion and latex preparation, they are also important in the control of the wetting and leveling characteristics of the applied paint. In painting applications that use lacquers such as the automobile industry, application and drying times are important. In such situations wetting and leveling are also important. In powdered lacquers, the presence of the proper surfactants produces a net electrical charge on the surface of the particles, which allows them to be applied quickly and evenly by electrophoretic processes. A potential drawback to rapid paint or lacquer application is that such speed can facilitate the introduction of air into the material resulting in foam formation at the time and point of application. If foam is produced, the drying bubbles on the painted surface will produce indentations and perhaps even bare spots that will significantly degrade the aesthetic and protective properties of the coating. To help prevent such foaming it is sometimes useful to add surfactants that also serve as antifoaming agents. Although it is common to relate surfactants with increased foam as in beer, shaving cream, whipped toppings, and firefighting foams.

1.7.6 Paper and Cellulose Products

Surfactants play several important roles in the papermaking industry. 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, require surfactants in their preparation. In addition, the water-absorbing capacity of paper is often controlled by the addition of the proper surfactants. Surfactants are also important in the process of recycling paper. A major step in the process is the removal of the ink and pigments present (deinking). That process is what is termed a flotation process in which a surfactant is added to aqueous slurry of old paper. The surfactant is chosen so that it will adsorb on the surfaces of pigment particle and ink droplets, causing them to become very hydrophobic. Air is then bubbled through the slurry. As the bubbles rise through the system, they become preferentially attached to the hydrophobic pigment and ink particles, acting like lifejackets and causing the particles to rise to the surface. At the surface they are skimmed off and separated from the cellulose slurry.

1.7.7. Mining and Ore Flotation

As just mentioned, the addition of the proper surfactant to a dispersion can produce a situation in which the solid particles, having a specific gravity much greater than that of water, can be made to float to the top and be easily (relatively speaking)separated from the aqueous phase. In the deinking mentioned above, there is no particular interest in being selective with respect to what is removed. It is essentially an ‘‘all out’’ proposition. In the mining industry the situation is quite different. The flotation process has been important in mining for much longer than has deinking. In many instances, the desired mineral is present in small amounts that would be difficult or impossible to isolate and process while still ‘‘mixed’’ with the bulk of the mined rock. In that industry, therefore, it is necessary to have a more selective flotation process in which the desired mineral can be separated from the bulk of the ore in a continuous and relatively inexpensive process. Because different

minerals tend to have slightly different surface properties, especially with regard to electrical charge characteristics, it is possible (with luck and perseverance) to design or formulate a surfactant system that will preferentially ‘‘float’’ a specific class of mineral while having little effect on other materials present. The selective surfactant or ‘‘collector’’ formulation allows the desired mineral to be skimmed from the top of the foaming slurry and thereby concentrated. The unwanted material can then be further processed or disposed of as slag. While the theory of the adsorption of surfactants onto solid surfaces is highly developed and well understood in ideal systems, the reality of the universe is that in such complex multi component systems as mining ores, theory soon runs out of steam and success ultimately depends on hands-on laboratory and field trials, intuition, and art (or perhaps black magic).Surfactants are also becoming more important in the coal mining industry. Aside from flotation processes, they are also employed as binders for the suppression of coal dust, and as dispersal aids and antifreezes for coal slurries that are pumped through pipelines.

1.7.8. Metal-Processing Industries

Surfactants are as important to the metal processing as to the mining industry. In order to perform as needed, metal surfaces must be cleaned and freed from deposits of oxides, oils, and other contaminants. Welding, painting, and other machining and surface treatments require a well-prepared surface. Even before that stage of fabrication, however, metals have a significant interaction with surfactants. High speed metal rolling processes, for example, require the use of lubricating and cooling emulsions. With increased rolling speeds, heat production and buildup become significant problems that could lead to damage to equipment and a loss in the quality of the finished product. Properly formulated

rolling oil emulsions containing surfactants reduce friction and the associated heat buildup, lessen the probability of rolling oils catching on fire, and help reduce the atomization of oil into the working environment and exhaust air. In cutting and machining operations, cooling lubricants are required to carry away the heat produced by the cutting and drilling operations, thereby protecting the quality of the work piece and prolonging the useful life of drill bits, and cutting surfaces. The components of cutting emulsions are critical, not only in terms of their direct action in metal processing but also because of worker and environmental exposure. The emulsions must be able to resist working temperatures in excess of 80C, they must have significant antibacterial properties since they are routinely used for extended periods open to the atmosphere, and their components must meet rigid toxicological, dermatological, and environmental requirements because of the degree of operator exposure during their use.

1.7.9. Plant Protection and Pest Control

Surfactants are critical components in agricultural formulations for the control of weeds, insects, and other pests in agricultural operations. The roles of surfactants are varied, ranging from their obvious use as emulsifiers in spray preparations to their role as wetting and penetration aids and, in some cases, as active pest control agents. Surfactants also improve application efficiency by facilitating the transport of the active components into the plant through pores and membrane walls. Foam formation during application can also be a problem since the presence of foam will, in most cases, significantly reduce the effectiveness of the applied material. In some applications, the choice of surfactant for a given active component can be critical. Since many pest control chemicals carry electrical charges, it is vital to use a surfactant that is electrically compatible with that ingredient. If

the active material is positively charged, the addition of an anionic surfactant can, and probably will, result in the formation of a poorly soluble salt that will precipitate out directly before being applied, or the salt will be significantly less active, resulting in an unacceptable loss of cost-effectiveness.

1.7.10 Foods and Food Packaging

There are at least two important aspects to the role of surfactants in food-related industries. One aspect is related to food handling and packaging and the other, to the quality and characteristics of the food itself. Modern food-packaging processes rely on high-speed, high-throughput operations that can put great demands on processing machinery. Polymer packaging, for example, must be able to pass through various manufacturing and preparation stages before reaching the filling stage, many of which require the incorporation or use of surfactant containing formulations. Bottles and similar containers must be cleaned prior to filling, processes that usually require some type of detergent. The detergent, however, must have special characteristics that usually include little or no foam formation. Low-foaming detergents and cleaners are also important for the cleaning of process tanks, piping, pumps, flanges, and ‘‘dead’’ spaces in the process flow cycle. The presence of foam will often restrict the access of cleaning and disinfecting agents to difficult areas, reducing their effectiveness at cleaning the entire system and leading to the formation of dangerous bacterial breeding grounds. In the food products themselves, the presence of surfactants may be critical for obtaining the desired product characteristics. Obvious examples would be in the preparation of foods such as whipped toppings, foam or sponge cakes, bread, mayonnaise and salad dressings, and ice cream and sherbets. Perhaps less obvious are the surfactants used in candies, chocolates, beverages,

margarines, soups and sauces, coffee whiteners, and many, many more. With a few important exceptions, the surfactants used in food preparations are identical or closely related to surfactants naturally present in animal and vegetable systems. Prime examples are the mono- and di-glycerides derived from fats and oils, phospholipids such as lecithin and modified lecithin, reaction products of natural fatty acids or glycerides with natural lactic and fruit acids, reaction products of sugars or polyols with fatty acids, and a limited number of ethoxylated fatty acid and sugar (primarily sorbitol) derivatives.

1.7.11 Chemical Industry

While surfactants are an obvious product of the chemical industry, they are also an integral part of the proper functioning of that industry. The important role of surfactants in the emulsion or latex polymer industry has already been mentioned. They are also important in other processes. The use of surfactants and surfactant micelles as catalytic centers has been studied for many years, and while few major industrial processes use the procedure, it remains an interesting approach to solving difficult process problems. A newer catalytic system known as phase transfer catalysis (PTC) uses amphiphilic molecules to transport reactants from one medium in which a reaction is slow or nonexistent into a contacting medium where the rate of reaction is orders of magnitude higher. Once reaction of a molecule is complete, the catalytic surfactant molecule returns to the nonreactive phase to bring over a new candidate for reaction.

1.7.12 Oilfield Chemicals and Petroleum Production

The use of surfactants in the mining industry has already been mentioned. It is in the area of crude oil recovery, however, that surfactants possibly stand to make their greatest impact in terms of natural resource exploitation. As the primary extraction of crude oil continues at its hectic pace, the boom days of easy access and extraction have begun to come to an end and engineers now talk of secondary and tertiary oil recovery technology. As the crude oil becomes less accessible, more problems arise with regard to viscosity, pressures, temperatures, physical entrapment, and the like. While primary crude recovery presents its technological challenges, secondary and tertiary recovery processes can make them seem almost trivial. Processes such as steam flooding involve injecting high-pressure steam at about340C into the oil bearing rock formations. The steam heats the crude oil, reducing its viscosity and applying pressure to force the material through the rock matrix toward recovery wells. Unfortunately, the same changes in the physical characteristics of the crude oil that make it more mobile in the formation also render it more susceptible to capillary phenomena that can cause the oil mass to break up within the pores of the rocks and leave inaccessible pockets of oil droplets. In such processes, surfactants are used to alter the wetting characteristics of the oil–rock–steam interfaces to improve the chances of successful recovery. Those surfactants must best able under the conditions of use such as high temperatures and pressures and extremes of pH. Although the use of surfactants for secondary and tertiary oil recovery is beneficial, it may also cause problems at later stages of oil processing. In some cases, especially where the extracted crude is recovered in the presence of a great deal of water, the presence of surfactants produces emulsions or micro-emulsions that must be broken and the water separated before further processing can occur. Naturally present surface-active materials in the crude

plus any added surfactants can produce surprisingly stable emulsion systems. The petroleum engineer, therefore, may find herself confronted by a situation in which surfactants are necessary for efficient extraction, but their presence produces difficult problems in subsequent steps.

1.7.13. Plastics and Composite Materials

The importance of surfactants in the preparation of polymer systems such as emulsion or latex polymers and polymers for textile manufacturer has already been mentioned. They are also important in bulk polymer processes where they serve as lubricants in processing machinery, mold release agents, and antistatic agents, and surface modifiers, and in various other important roles. Surfactants can also play an important role in the preparation of composite materials. In general, when different types of polymers or polymers and inorganic materials (fillers) are mixed together, thermodynamics raises strong objections to the mixture and tries to bring about phase separation. In many processes, that tendency to separate can be retarded, if not completely overcome, by the addition of surfactants that modify the phase interfaces sufficiently to maintain peace and harmony among normally incompatible materials and allow the fabrication of useful composites.

1.7.14. Pharmaceuticals

The pharmaceuticals industry is an important user of surfactants for several reasons. 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 important in

terms of aiding in the passage of active ingredients across the various membranes that must be traversed in order for the active ingredient to reach its point of action. They are also important in the preparation of timed-release medications and transdermal dosification. And in some cases, surfactants are the active ingredient. Surfactants for the pharmaceuticals industry must, of course, meet very rigid regulatory standards of toxicity, allergenicity, collateral effects and so on.

1.7.15. Medicine and Biochemical Research

Living tissues and cells (we and everything we know included) exist because of the physicochemical phenomena related to surface activity—in a sense, natural surfactants could be considered essential molecular building blocks for life. They are essential for the formation of cell membranes, for the movement of nutrients and other important components through those membranes, for the suspension and transport of materials in the blood and other fluids, for respiration and the transfer of gases between the atmosphere (the lungs, in our case) and the blood, and for many other important biological processes. It should not be surprising, then, that surfactants are finding an important place in research into how our bodies work and processes related to medical and biochemical investigations. Their roles in cosmetics and pharmaceuticals have already been mentioned, but their importance in obtaining a better understanding of life processes continues to grow. It is very probable that the years ahead will bring some surprising biochemical results based on surfactants and surface activity.

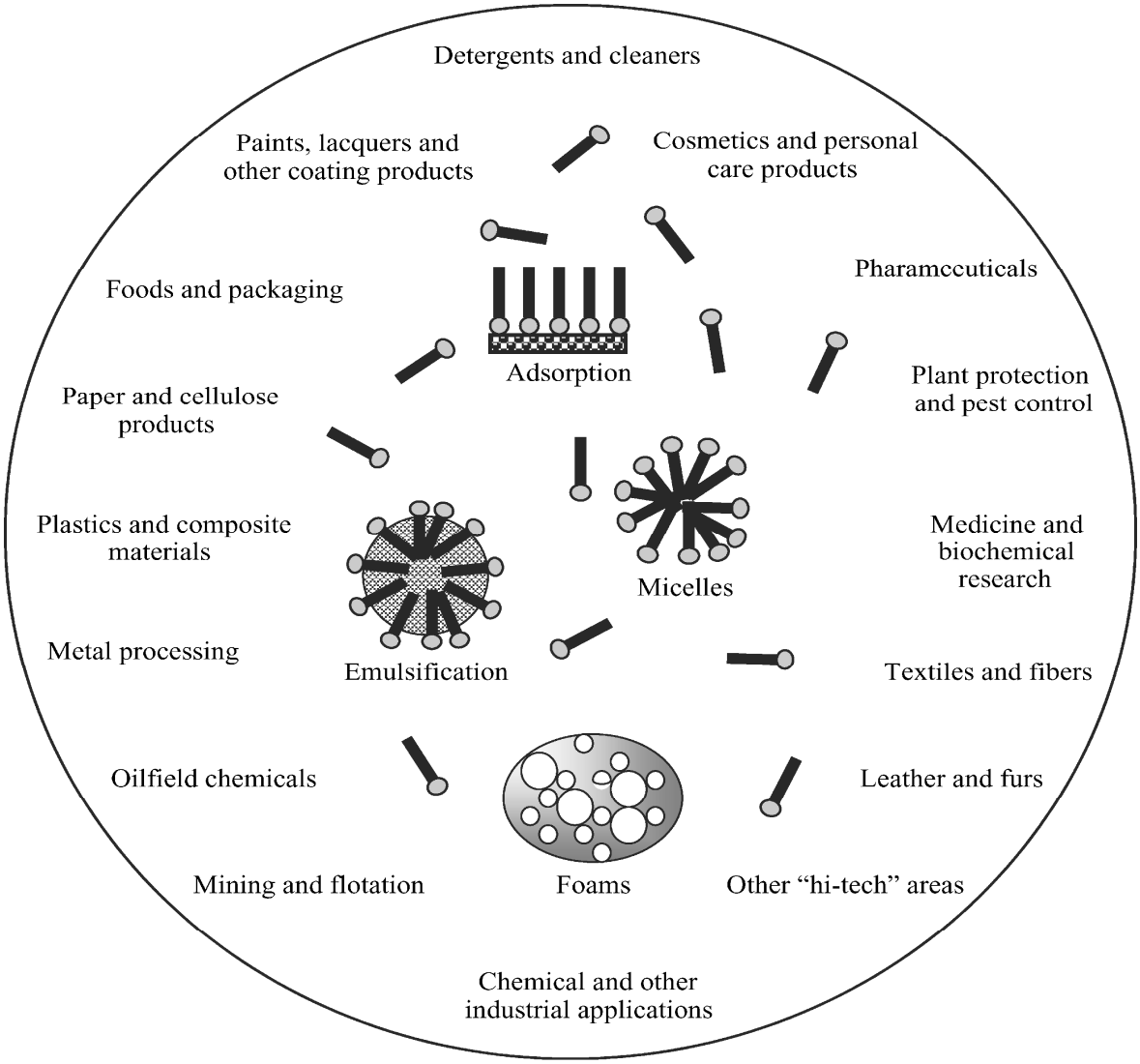


Figure 1.4: Fields of application of surfactant in different sectors

1.8 SOLUBILIZATION

In the previous section we have been mainly concentrating on two-component system water-surfactant. Non-trivial effects are often found when one or more additional components are added to such a two component system. The particular phenomenon that occur depend on the chemical nature of the additives. Is the additive anon-polar substance that is practically insoluble in pure water, the solubility itself, tresses dramatically when the surfactant concentration reaches the CMC? This is due to solubilization of the additive in the micelle. When the added component is an amphiphile itself, the CMC can change substantially and the resulting aggregates are best described as mixed micelles. The distinction between a-polar and amphiphilic additives is not sharp, and for example, long chain alcohols have intermediate propertied. The added component can also have potential chemical reactivity. It is often found that the reaction rate substantially affected by the presence of micelles. This is called micellar catalysis and is an area of research that has attracted much attention in recent years. Probably the most significant property of micellar solution from a technical and biological point of view is their ability to dissolve substances that are insoluble in pure water. For example, detergent activity of an ordinary soap is partly due to the solubilization ability of micelles. The mechanism for the solubilization is conceptually most easily understood within phase separation model. At surfactant concentration above the CMC, the micelle form a pseudo-phase and solute partitions between the micellar aqueous phases. An a-polar solute highly favors the micelle due to their liphophilic interior. An increase in surfactant concentration will thus lead to an increase in the solubility of the additive. It is clear from this description that the solubilization is not due to specific binding to a site on or in the micelle but it is rather like a non-specific dissolution in a non-aqueous phase. This conclusion is further supported by

spectroscopic observations using NMR[75], ESR[76], fluorescence depolarization[77]and which show that the solubilizate moves in a liquid-like environment with no sign of direct association with a specific surfactant molecule. With the use of small system thermodynamics[78,79] one can put the phase separation treatment of solubilization into a formally rigorous framework[80-83]. One important of a result of such a formulation is the proof relation analogous to Henry's law[18]

$C_{cmc}(X_A)=cmc(X_A=0)-kX_A$……(1.16)

Where cmc is the surfactant concentration when micelles start to form and X_A is the mole fraction of the additive. This relation has been experimentally verified with alcohols as additives. For many a-polar solutes of course the attainable X_A is so small that it is difficult to detect any effects on the CMC. Much effort has been made to determine the location of a solubilizate within the micelle[84]. It is essential to remember that the solubilization phenomenon is analogous to dissolution in a non-aqueous phase. It then follows that there is no distinct solubilization site. However, an additive has different affinities to different part of the micelle, and it is distributed within the micelles according to these affinities. In experimental studies of solubilization the measured quantities are averages, of one type or the other over this distribution. Both from the general principle that govern micelle formation and from direct experimental investigations[85-88], it seems that molecules with a polar group are solubilized close to the micelle-water interface; presumably with the a-polar part of the molecule sticking into the micelle core. Aliphatic hydrocarbons, on the other hand, are preferentially solubilized in the interior of the micelles. For aromatic compounds the picture is less clear and there has been a considerable controversy about dynamic solubilization site[85,89-92]. However, the most recent studies[93,94] indicate that aromatic compounds are preferentially solubilized close to the micelle-water interface.

From a thermodynamic point of view there are several factors that influence the distribution of a solubilizate within a micelle. In addition to the direct solute-water, solute-alkyl chain, and solute-polar group interactions, it is important to consider that a solubilizate influences the packing of hydrocarbon chains in the micelle. Due to the curved surface of the micelles, solubilization close to the micelle surface will decrease the amount of gauch conformation in the surfactant alkyl chain, which leads to gain in energy. Alternatively will a solubilizate at the micelle surface expel water molecules and decrease the hydrocarbon-water contact area. The difference between aromatic and aliphatic solubilizates with regard to their location in the micelles might be caused by a tendency of the rigid planer aromatic rings to disturb the packing of the alkyl chains. Additional thermodynamic information on solubilization is obtained by measuring solubility of non-polar additives in the micellar solutions. In such measurements, one should ensure that the micellar phase saturated in solute is in equilibrium with pure solute, either crystalline or liquid, since otherwise the interpretation of the data is complex. For homologous series of surfactants it is found that the solubilities of non-polar additives increase with increasing alkyl chain length of the surfactant[95-97]. Bridi[80,81] found that the mole fraction additive X_m within the micelle at saturation increases exponentially with the number, n, of $-CH_2-$ group in the surfactant. This n-dependence of X_m was interpreted[80,81] as due to the hydrophobic interaction, but the argument in favor of such an interpretation seems unclear. Already in 1938, Hartly[98,99] suggested that the increase solubilization ability with increasing n is correlated with the increase in micellar size. This idea is corroborated by the data of Jacobs[97], which show that for the same surfactant ion the solubilization ability increases when the micellar size is increased by changing the counter-ion. If Hartley suggestion is correct, it remains to explain why a larger micelle is more effective in solubilizing an

additive than a small micelle. That the solubilization of a solute in a micelle can be quantitatively different from dissolution in a pure solvent was nicely demonstrated by Larson and Magid[100] who measured the enthalpies of dissolution of a number of solutes in a CTAB solution. For *n*-hexane and cyclohexane, the heat of transfer from water to the micelle was small and positive as expected for a process driven by the hydrophobic interaction. Similar results were found for a number of slightly polar salts like butyric acid, 2-butanon and uracil. However, for benzoic acid and its derivatives, as well as for phenols large up to -25KJ/mole-negative heats of transfer were consistently found. The measured heats of solution in the micellar solutions for these compounds do not show any resemblance to those found in pure water or in pure hydrocarbon. This observation again indicates that these solutes are solubilized in the interface between the water and the a-polar interior of the micelle. The general view of a reduced water-hydrocarbon contact on micelle formation has been discussed schematically from thermodynamic and kinetic properties of micelles, a much more refined picture must be available. Specific questions have to be answered concerning the free monomer hydration, water penetration into micelles and hydration of the polar heads. For ionic amphiphiles, one must consider the counter-ion hydration and closely related problem in this case concerns counter-ion-micelle interactions. The properties of water in wide range of environments is a field of intense research and a most useful account for the actual state of knowledge for a multitude of systems ranging from pure water to complex heterogeneous systems may be found in Frank's series "Water"[101].

1.9 AIM AND OBJECTIVE OF THE PRESENT WORK

Surfactants are used in many industrial applications; however do not work effectively below a certain critical temperature known as the critical micelle temperature or Krafft temperature (T_k). The T_k value is generally interpreted as the melting temperature of hydrated solids above which an abrupt change in solubility of ionic surfactants occurs. The T_k values are found to increase with increasing the length of alkyl chain and decrease with increasing the size of the head-group. This probably explains why traditional surfactants bear a hydrocarbon chain usually shorter than C_{18} in order to ensure their sufficient water solubility and the capacity of micelle formation for their practical use. Below the T_k value, hydrated crystalline solids start to separate when the surfactant concentration exceeds saturated dispersion of the monomeric form. Under this condition, the surfactant loses its surface active nature, detergency, emulsifying and micelle forming properties. Therefore, it is essential to lower the T_k value of surfactants below room temperature for their wider industrial applications. Addition of inorganic electrolytes is found to lower the CMC values of surfactants and enhances the surface activity, which definitely favors their practical use since many industrial applications of surfactants lie on their capacity of micelle formation[102,103]. Extensive research work has been dedicated to the effect of alkyl chain length, head-group size, and different additives on the T_k and CMC values of ionic surfactants[102-108]. These studied have revealed that the CMC values decrease while T_k values increase with an increase in the concentration of electrolytes. The decrease in CMC values with an increase in the salt concentration has been attributed to the reduction in the electrostatic repulsion that arises from the screening of the effective head charge of the surfactant [108-112]. In the case of zwitterionic surfactant, the T_k values were found to depress significantly upon the addition of NaCl and this phenomena has been attributed to the

influence of added electrolytes on the structure of water[104,105]. Despite extensive studies on micellization of ionic surfactants in the presence of counter-ions, detailed investigation regarding their thermodynamics of micelle formation and adsorption along with the depression of the T_k value in the presence of added electrolytes are sparse. Keeping this in mind, we have endeavored to present the thermodynamics of surface adsorption and bulk micellization along with T_k values of CTAB and TTAB in pure water and in aqueous NaCl solution. In the present study, we have observed that in the case of these surfactants, the T_k value decreases significantly as observed for some zwitterionic surfactants with an increase in the concentration of NaCl favoring their applications from solubility viewpoint. In addition, we have studied the adsorption and micellar behavior of CTAB and TTAB over a wide range of temperature in the absence and presence of NaCl. It needs to be mentioned here that while in pure water the CMC values increase slowly with increasing temperature those in presence of added electrolytes initially increase and then decrease gradually with an increase in temperature as observed in the case of some nonionic surfactant[4,7]. Thus the CMC vs. temperature plot can be represented by a Λ-shaped curve. There are sharp contrasts to the usual behavior of ionic surfactants and to the best of our knowledge no reports concerning the depression of T_k values and Λ-shaped curve for temperature dependence CMC values of classical ionic surfactant in presence of NaCl have appeared in the literature. The experimental findings correlated with the thermodynamic parameters for adsorption and micelle formation would extend our knowledge regarding surface and bulk behavior of surfactants in aqueous solution. Moreover, a water insoluble dye, sudan red B (SRB) was solubilized in aqueous micellar solution of CTAB and TTAB in the absence and presence of NaCl. From these studies we can piece together an explanation of how the surface and bulk properties of the surfactant in both pure water and in aqueous NaCl

solution are influences by the change in temperature and why the presence of NaCl paves the way for wider use of CTAB in terms of its higher surface activity, lower CMC and depressed T_k values.

2.1 CHEMICALS

The surfactant CTAB and TTAB was supplied by Sigma, Aldrich, with a purity of > 99% and was used as received.

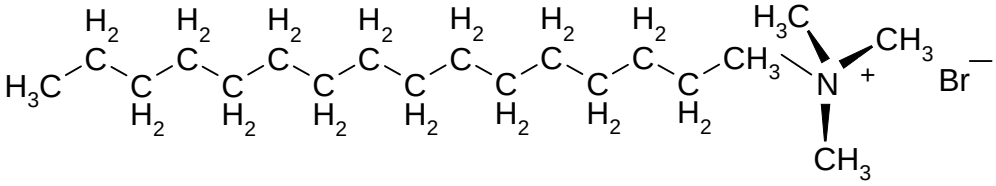


Figure 2.1 Structure of Cetyltrimethylammonium Bromide(CTAB)

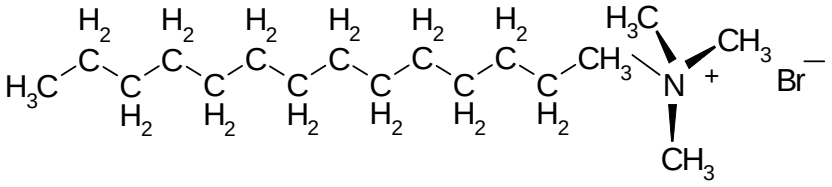


Figure 2.2 Structure of Tetradecyltrimethylammonium Bromide (TTAB)

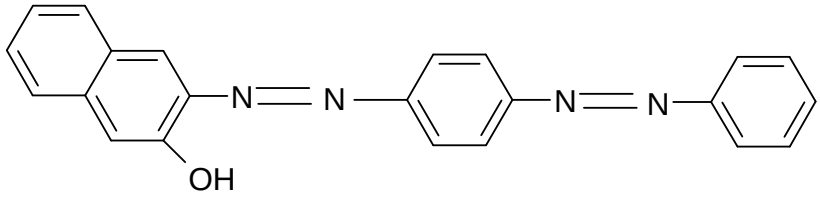


Figure: 2.3: 1-((4-(phenyldiazenyl)phenyl) azonaphthalen-2-ol(Sudan Red B)

Analytical grade NaCl, Ethanol obtained from Merck,Germany was used as received. Double distilled water was used for the preparation of all the solution.

2.2 KRAFFT TEMPERATURE (T_k)

2.2.1 Conductometric Method

To measure the T_k value of the surfactant in pure water and in aqueous NaCl solution, 4×10^{-3} CTAB and TTAB solution was prepared and place in a refrigeration for 24h at about 4^oC. Under this condition precipitation of the hydrated surfactant occurred. The system was then taken out of the refrigerator and the temperature of the precipitated system was raised at a rate of 1^o C/10 min under the condition of gentle stirring. For each temperature, conductivity of the solution was checked several times until it reached a steady value. The T_k value was then taken as the temperature at which a sharp break in the conductivity vs. temperature plot occurred.

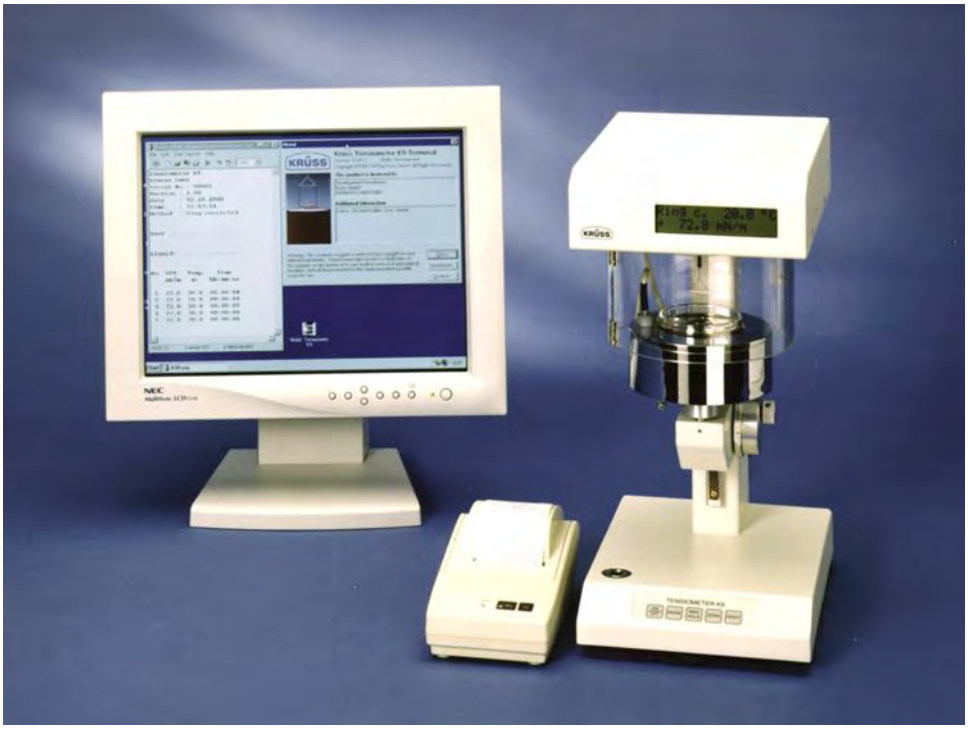


Figure 2.4: Kruss K 9 (Surface Tensiometer)

Figure 2.5 : EUTECH-CyberScan-CON-510 (conductivity meter with a temperature-compensate cell)

2.3 MEASUREMENT OF CMC

2.3.1 Surface Tensiometric Method

For CMC measurements, the surface tension of the aqueous surfactant solutions of different concentrations were measured by a surface tensiometer (Kruss K 9) equipped with a platinum plate. The solution was transferred into a vessel that was thermostated by circulating water of desired temperature. The surface tension measurements were started with a dilute solution and the subsequent concentrated solutions were made by adding previously prepared stock solution into vessel. The establishment of equilibrium was checked by taking a series of reading after 10-min intervals until no significant change occurred. The accuracy of these measurements was within ±0.1mN/m. Details of the experiment procedure are to be found elsewhere[4].

2.3.2 Conductometric Method

Conductivity measurement was carried out by using a EUTECH-CyberScan-CON-510 conductivity meter with a temperature-compensate cell (cell constant provided by manufacture is 1.0 cm^{-1}). The conductivity meter was calibrated by measuring the conductivity of the solution of potassium chloride (Merck, purity>99%) of different concentration (0.001, 0.01 and 0.1M). the cell was equipped with a temperature sensor with a resolution of ±0.1K. Experiments were started with a dilute solution and subsequent concentrated solution was obtained by adding a previously prepared stock solution into a 50 mL beaker. The temperature of the solution was kept constant by using a circulating water bath (HAAKE B 3, Germany) with a precision of 0.1K. To observe the effect of

NaCl solution on the CMC of solution, surfactant solution was prepared in the NaCl solution of particular concentrations.

Figure 2.6: HAAKE B 3, Germany ,A CIRCULATING WATER BATH

2.4 SOLUBILIZATION

2.4.1 UV-vis Spectroscopic Method

A UV–vis spectrometer (SHIMADZU UV spectrophotometer model UV-1601PCS) was used to study the micellar solubilization of sudan red B in CTAB and separately in TTAB solution in pure water and in the presence of NaCl. The absorbance of each solution was measured by using a pair quartz cell of path length 1 cm. The concentration of Sudan Red B in CTAB and TTAB micelles wascalculated from

calibration curve obtained from the absorption spectra of known concentrations (1×10^{-3}-8.0×10^{-3} mM) of SRB in ethanol against a blank. The strong absorbance at λ_{max}=512.5nm gave a satisfactory Beer's law plot. Solubilization studies were conducted using the maximum solubilization at a constant temperature of 30^{o}C. The surfactant concentrations were varied from below CMC to about four times the CMC. The fixed amounts of solute

Figure 2.7: SHIMADZU UV spectrophotometer model UV-1601PCS

were added to maintain excess product at least three times its solubility limits after achieving solubilization equilibrium. The solubilization studies were conducted in 100mL reagent bottles. The solutions were equilibrated by shaking for 48 h with the help of mechanical shaker and then centrifuged at 3000 rpm for 15 min by a centrifuge machine (HETTICH Universal 16A). The supernatant was removed and analyzed for the bulk surfactant concentrations through UV spectroscopy.

Figure 2.8: HETTICH Universal 16A (A CENTRIFUGE MACHINE)

3.1 EFFECT OF NaCl ON KRAFFT TEMPERATURE

Figure 3.1 and 3.2 show the Krafft temperature (T_k) in pure water and in presence of NaCl for CTAB and TTAB respectively. The T_k values of CTAB and TTAB were found to be 24.8^o C and 12^{o}C respectively. The values are found to be in good agreement with the literature value [25]. It is important to note here that the T_k value of CTAB is higher than that of TTAB. This is due to the fact that T_k values increase with increasing the length of hydrophobic alkyl chain. These values are in good agreement with the literature value[109,110]. Usually, addition of electrolytes reduces the CMC of surfactants which favors their practical use. However, added electrolytes enhance the T_k values, which is obviously unfavorable for industrial applications. The T_k values of a number of ionic surfactants have been measured in the presence of added electrolytes[20,21,24-26].The T_k values of some common surfactants in water and in electrolyte solution are given in Table 3.1. These studied have revealed that the T_k values increase with an increase in the concentration of added electrolytes. For example, the T_k value of CTAB increases from 24^{o}C to 34.6^{o}C when the NaBr concentration is 0.5 mol/kg[20]. Similar behavior has been observed of hexadecyl pyridium surfactants in the presence of electrolytes having anions common to the anionic counterparts of the surfactants[21]. On the other hand, a depression of T_k values has been reported for a series of some zwitterionic surfactants in the presence of NaCl [22,23]. As shown in Table 3.1, the presence of the Br^- ion result in an increase in the T_k value of CTAB while the presence of Cl^- ion lowers the T_k values of the same surfactant as observed in the present work. Here, we have observed that the T_k value of CTAB decrease from 24.8^{o}C in pure water which to 16^{o}C in the presence of 0.01 M NaCl solution (Figure 3.1). In figure 3.2, the T_k value of TTAB in pure water is 12^{o}C which decrease in 10.5^{o}C

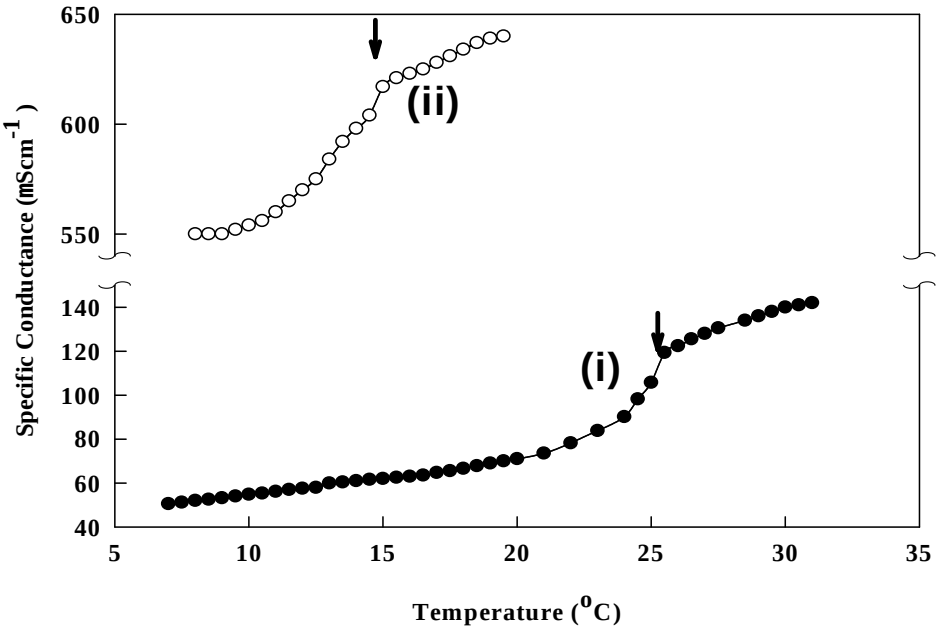


Figure 3.1: Krafft temperature of CTAB (i) pure water and (ii) in presence of 0.005 M NaCl solution

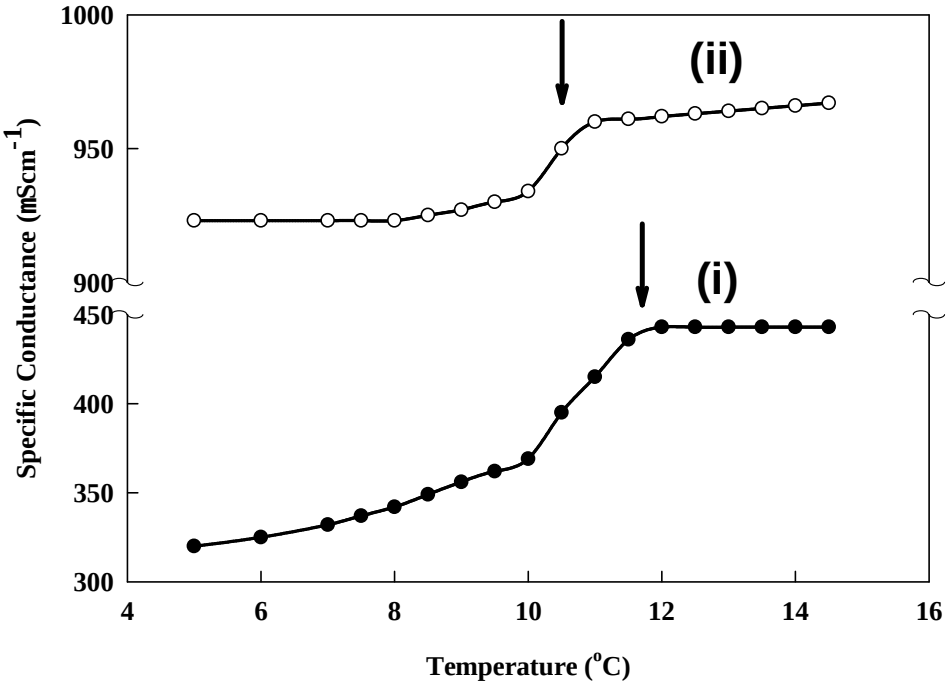


Figure 3.2: Krafft temperature of TTAB (i) pure water and (ii) in presence of 0.005 M NaCl solution

Table: 3.1: Krafft Temperature of some common ionic surfactants including CTAB and TTAB in absence and present of salt.

Surfactant	Added Salt	Salt concentration	T_k(^oC)	Source
CPC	Nill	0.000	11.25	Ref. 21
	KCl	0.100	19.20	
SDS	Nill	0.000	14.36	Ref. 25
	NaCl	0.020	16.25	
CTAB	Nill	0.000	24.80	This work
	NaBr	0.012	26.70	Ref. 115
	NaBr	0.500	34.60	Ref. 20
	NaCl	0.005	20.00	This work
	NaCl	0.010	16.00	
TTAB	Nill	0.000	12.00	This work
	NaCl	0.005	10.50	
	NaCl	0.010	10.00	

CPC- Cetylpiridinium Chloride, **SDS**-Sodiumdodecyl Sulphate

in presence of 0.005M NaCl solution. While the CTAB and CPC (cetylpyridium chloride) are found to increase in presence of the $Br^-$and Cl^- ions, respectively the T_k values of both CTAB & TTAB decrease in the presence of the Cl^- ion. Although, all these ions are structure breakers, the concept of structure breaking or structure making properties of ions cannot satisfactorily explain the dependence of the T_k values of CTAB & TTAB on the

concentration of the Cl^- and Br^- ions. To explain the influence of the Cl^- and Br^- ions on the T_k value of the surfactants, we have to consider the structure breaking and salting-in behavior of the ions along with the contact ions effect on the solubility of the surfactant simultaneously. According to Collins's concept[117]of matching water affinities, cheotropes can form direct ion pairs with other chaotropes. In other words, large anions having low charge density have the propensity to pair with large cations when their water affinities are similar. Applied to CTAB, this means that SCN^- and I^- ions will form closest ion pair with the alkyltrimethylammonium ion. Since both SCN^- and I^- are weakly hydrated ions, their pairing with alkyltrimethylammonium ion lead to contact ion pairs with low solubility (compare: CsI is much less soluble than LiI). As a consequence, these ions are more effective in screening in the electrostatic repulsion between the alkyltrimethylammonium bromide molecules. Furthermore, more weakly hydrated ions such as SCN^- and I^- have higher tendency to accumulate at the air-water and hydrocarbon-water interfaces and directly disturb the hydrophobic hydration around the hydrocarbon moiety[117,118]**.** As a result, they promote salting out behavior, leading to an increase in the T_k value (visual observation) of the surfactant. Such a salting out behavior of lysozyme in the presence of strong chaotropes has been observed previously[118]. From simulation study Hayda et al[119]reported that as the chain length of tetraalkylammonium ion increases, pairing with more chaotropic ion is increasingly preferred over that with less chaotropic ions exhibiting a reversal of the Hofmeister effect. Our experimental is in line with this phenomenon. As ions get smaller and their charge density increases, they typically have more tightly bound water molecules in the hydration sphere. Therefore less chaotropic Cl^- ion exhibit higher tendency for hydration than SCN^- and I^- ions[120]**.** It has been reported that when an ion is strongly hydrated than its oppositely charged partner dehydrating the more strongly

hydrated ion and cost more its energy than it can gain by forming a contact ion pair with more weakly hydrated ions[121]. Therefore, these ions will tend to stay apart rather than forming contact ion pairs with the cationic part of the surfactants. Nuclear magnetic resonance study showed that the water molecules adjacent to a chaotrope tumble more rapidly than in the bulk solution as expected for water a molecule which is not held by its neighbors[122]. Therefore, the presence of Cl^- increases the concentration of free water molecules and promotes hydration of CTAB and TTAB molecules. As a result, the solubility of the surfactants increases in the presence of the ion resulting in a decrease in the T_k value. It is well-known that when a solution contains a poorly soluble salt in equilibrium with its ions, an increase in the concentration of one of the ions will cause a corresponding decrease in the concentration of the other ion to maintain the constant value of the solubility product of the ions present in solution. Thus, to maintain constant value of the solubility products, the solubility of CTAB in the presence of the Br^- ion decreases, showing an increase in the T_k values of the surfactant. On the other hand, more weakly hydrated anions are excluded to a lesser extent from the air-water and hydrocarbon-water interfaces and directly disturb the hydrophobic hydration around hydrocarbon moieties[118,123]. When added the salt contains an ion common to that of the surfactant such as Br^- in CTAB[126] or Cl^- in CPC[117]solutions, probably the common ion effect dominates over the salting-in effect. It is well known that if a solution contains a poorly soluble salt in equilibrium with its ions, it is to be expected that an increase in the concentration of one of the ions will cause a corresponding decrease in the concentration of the other ion to maintain the constant value of the solubility products of the ions present in solution. Thus to maintain constant value of the solubility products, the solubility of CTAB and TTAB in

the presence of the Br^- or CPC in the presence of the Br^- ion decrease, showing an increase in the T_k values of the surfactants.

3.2 SURFACE ADSORPTION AND BULK MICELLAR BEHAVIOR OF THE SURFACTANT

The CMC value of CTAB and TTAB at a definite temperature was measured by tensiometric and conductometric methods. The CMC values were found to agree within 1-2% for all the calculated data. Typical experimental illustrations are shown in Figures from 3.3 to Figure 3.10. Spontaneous adsorption of surfactant molecules from the bulk of the aqueous solution to the solution surface results in a decrease in the surface tension (γ) with an increase in surfactant concentration. Figures from 3.3 to 3.6 show the representative γ vs. $\log_{10}C$ plot at different temperatures of CTAB and TTAB. It is evident from these figures that near the CMC value the rate of decreasing in γ values is small and then the values remain almost constant with further increase in the bulk concentration of the surfactant because of saturation of the solution surface by the adsorbed molecules. The CMC has been determined from the intersection of the γ vs. $\log_{10}C$ plot. Moreover, during surfactant-salt solution surface tension vs. concentration plot shows the same trend as shown in Figures 3.5 and 3.6 of CTAB and TTAB respectively. Since CTAB possesses larger alkyl chain than the TTAB, at a definite temperature the CMC values of CTAB are found to be lower than the corresponding values of TTAB. Figures 3.7, 3.8, 3.9 and 3.10 show the specific conductance (κ) vs. surfactant concentration plots in both pre- and post-micellar region, the slope of pre-micellar region being greater than that of the post-micellar region. It is observed that the κ values gradually increase with an increase in concentration

of surfactant solution. This may be attributed to an increase in the number surfactant monomers in solution with increasing concentration. The break point in the conductance vs. concentration curve indicates a sharp increase in the mass per unit charge of the surfactant system in solution and is explained as the evidence of the formation of the micelles from the monomeric surfactant molecules with part of the charge of the micelle neutralized by the associated counter-ions. The intersection point between two slopes indicates the CMC of the surfactant. The CMC values obtained from the surface tensiometric and conductance methods are found to agree with the literature values[125,126]. The equilibrium surface tension(γ_{CMC}) values are found to be higher with increasing temperatures for aqueous surfactants solution. On the other hand, in presence of salt (0.01M NaCl) the trend is same for the surfactants solution. The increase of γ_{CMC} values of surfactant solution with temperature, suggests the gradual decrease in surface excess concentration(Γ_{max}) of the adsorbed molecules. Due to increase in temperature, both the molecular motion and chain flexibility increase and results a poorer packing of the molecules in adsorbed monolayers in absence and in presence of salt in surfactant solution. Comparably, the γ_{CMC} values of the cationic surfactants (CTAB and TTAB) are lower in salt solution than in the aqueous solution. The added electrolytes neutralize the charge of the surfactant head group. As a result, the electrostatic repulsion between the head-group is substantially minimized. Under this circumstance, the adsorbed molecules attain a closer molecular packing showing a lower γ_{CMC}value in the presence of NaCl compared to the corresponding value in pure water. Moreover, the γ_{CMC} values for pure CTAB are found to be higher than that of pure TTAB. It is a reason for their distinguishable chain length because CTAB contains two more – CH_2 – than the TTAB. Additionally, in the presence

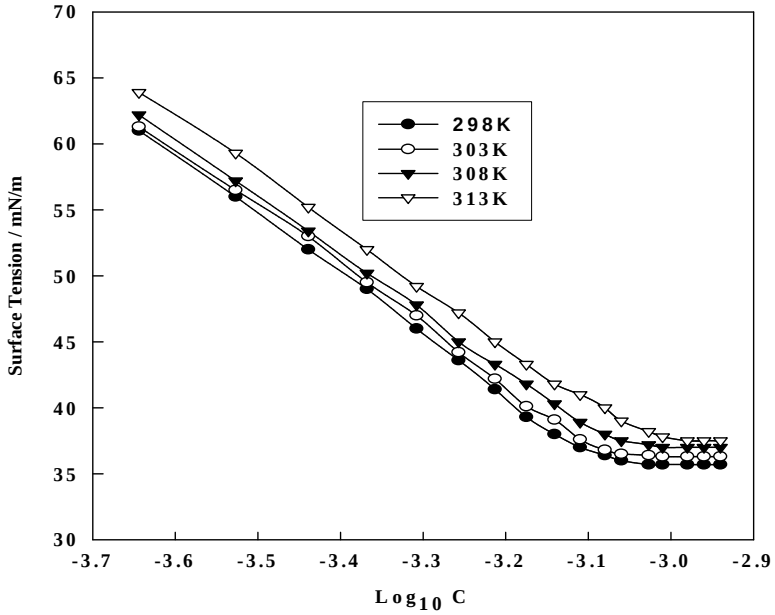


Figure 3.3: Surface tension vs. Log_{10}Cof various CTAB solutions at different temperatures.

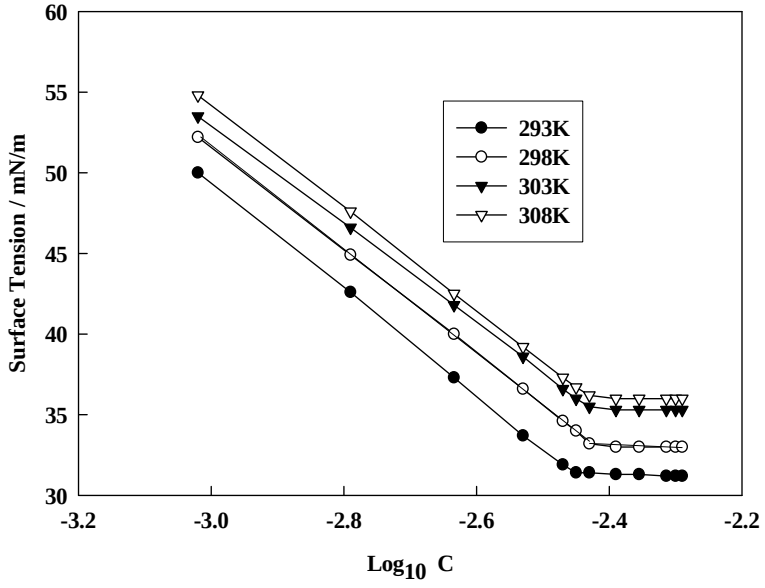


Figure 3.4: Surface tension vs. Log_{10}Cof various TTAB solutions at different temperatures.

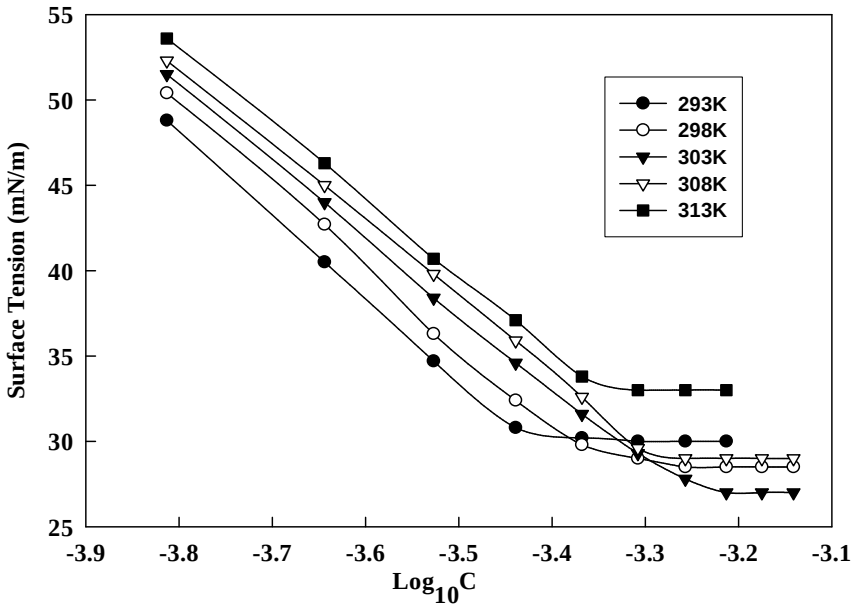


Figure 3.5: Surface tension vs. $Log_{10}C$ of CTAB-0.01M NaCl solution in different temperatures.

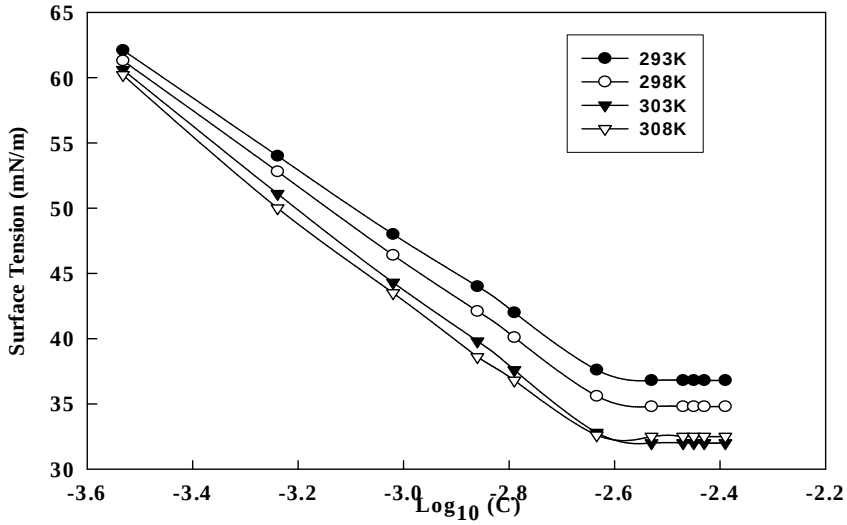


Figure 3.6:Surface tension vs. $Log_{10}C$ of TTAB-0.01M NaCl solution in different temperatures

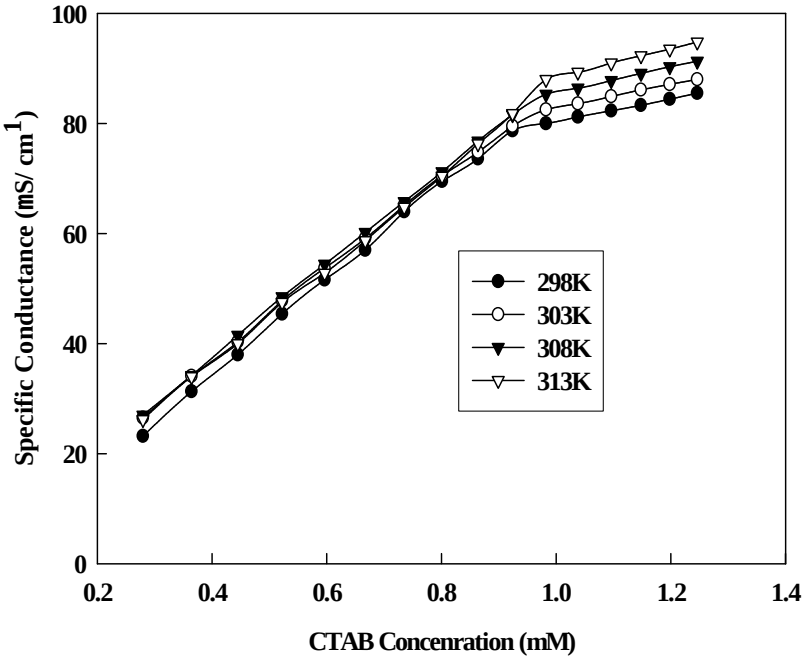


Figure 3.7: Conductance vs. surfactant concentration plot for CTAB in aqueous solution at different temperatures

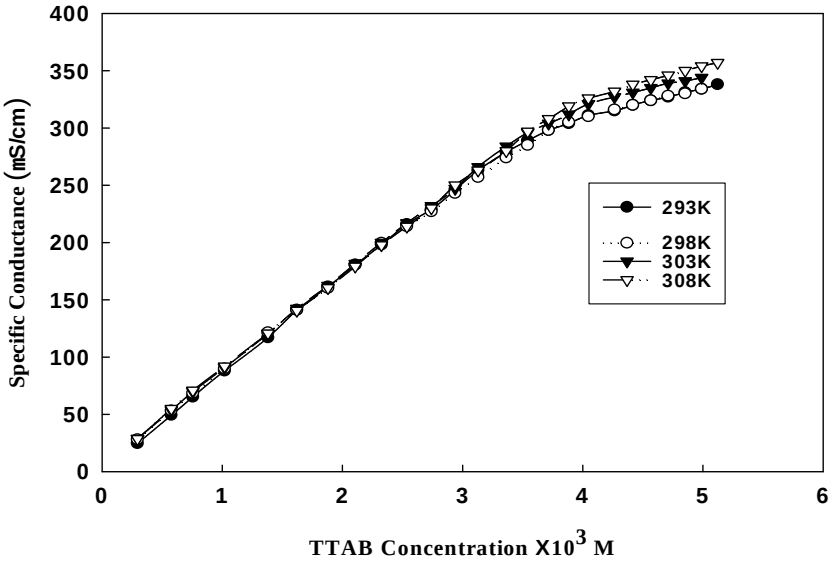


Figure 3.8: Conductance vs. surfactant concentration plot for TTAB in aqueous solution in different temperatures

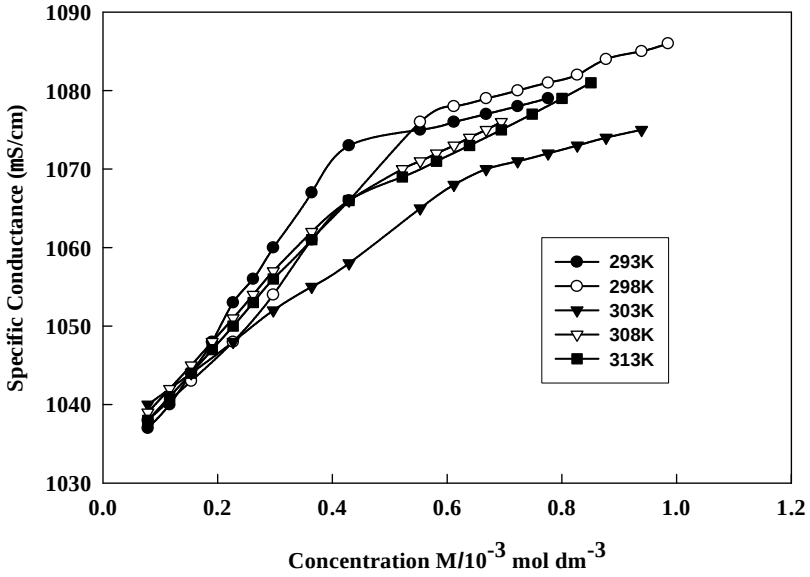


Figure 3.9: Conductance vs. concentration of CTAB-0.01M NaCl in different temperatures

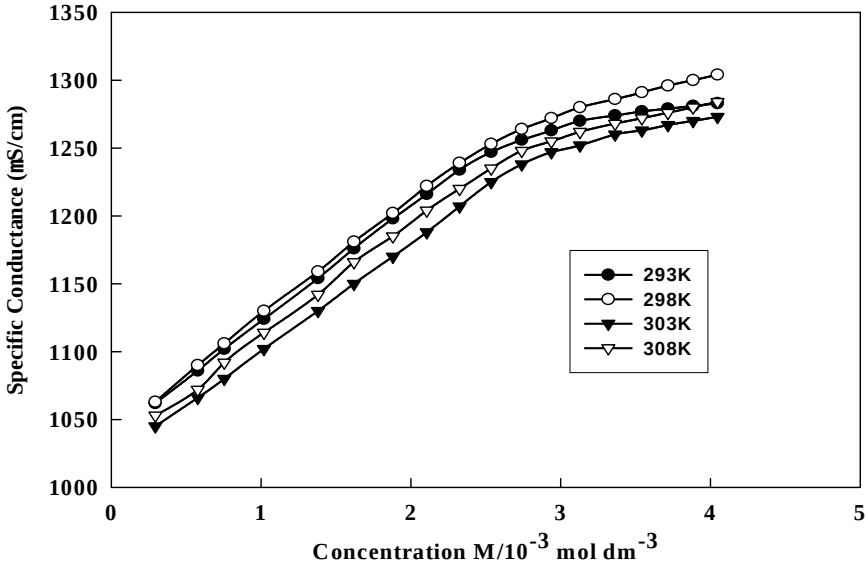


Figure 3.10: Conductance vs. concentration of TTAB-0.01M NaCl in different temperatures.

of NaCl the surfactants show the same activity upon increasing the temperatures. Figures 3.11 and 3.12 show the variation of CMC values with temperature in pure water and in aqueous NaCl solution for both CTAB and TTAB, respectively. It is evident from the Figure 3.2 that in pure water the CMC values of the surfactants increase with increasing temperature over the studied temperature range. At a definite temperature, the CMC value of a surfactant is governed by the balanced interaction of the van der Waals forces between the hydrophobic alkyl groups that have a tendency to stabilize the micelle and the opposing repulsive interactions between the head groups that have a tendency to split up the micelles. Again, two opposing thermally controlled effects should be considered simultaneously to gain insight into the temperature dependence of CMC. These are: (1) disruption of the water structure surrounding the hydrophobic group which disfavor micellization and lead CMC to higher values and (2) decrease in the degree of hydration of the head group that imparts hydrophobic nature of the surfactant, which favors micellization and leads the CMC to lower values. Our experimental results reveal that the CMC values of CTAB and TTAB in pure water show an increasing trend with an increase in temperature as shown in Figures 3.11 and 3.12 respectively, indicating that the first effect predominates over the second one within the studied temperature range. Quite different trend of the temperature dependent CMC values of CTAB and TTAB was observed in NaCl solution. A significant number of papers have dealt with the effect of electrolytes on CMC values of ionic surfactants[25-28,125,126]. These studies have shown that CMC values decrease in the presence of added electrolytes which has been attributed to screening of the surface charge by the counter-ion. For example, in presence of 0.05M NaBr the CMC of CTAB at 298K found to be 0.12mM and in 0.01M NaCl the CMC of CTAB at 298K found to be 0.15 mM where in pure water at the definite temperature the

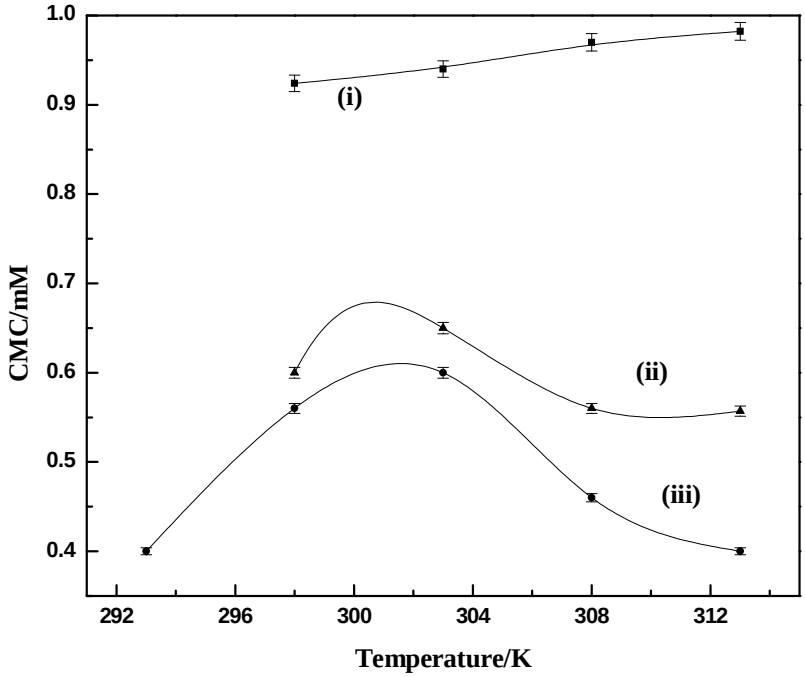


Figure 3.11: Dependence of CMC values of CTAB in (i) pure water and (ii) 0.005M (iii) 0.01M aqueous NaCl solution with temperature.

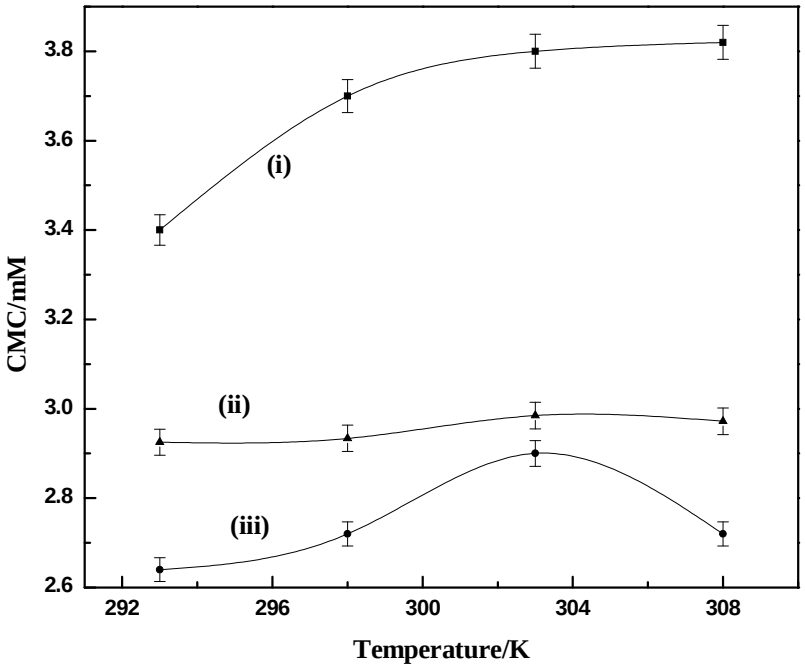


Figure 3.12: Dependence of CMC values of TTAB in (i) pure water and (ii) 0.005M (iii) 0.01M aqueous NaCl solution with temperature.

CMC of CTAB is found to be 0.97 mM[127]. It is interesting to note here that in presence of NaCl the CMC values both of the surfactants initially increase and then decrease with an increase in temperature showing a maximum at 27^{o}C for CTAB and 30^{o} C for TTAB. This is a sharp contrast to the usual behavior of cationic surfactants and was observed for some typical non-ionic surfactants having small head group[4]. Low CMC values of the surfactant in NaCl solution can be attributed to neutralization of the charge of micelle surface by the excess counter-ion and thereby reduction in the repulsive force between the head groups in the presence of NaCl. The initial increase in temperature brings about an increase in the CMC value of the surfactant. An increase in CMC value can be attributed to an increase thermal solubility of the surfactant molecules with increasing temperature in the presence of NaCl. At 27^{o} C for these two effects offset each other, and then the dehydration of the head-group dominates over the solubility effect. Under this condition the surfactants show maximum CMC values in the CMC vs. temperature curve. For CTAB and TTAB, the temperatures 27^{o}C and 30^{o}C are found respectively. As a result, steric hindrance between the head-groups of the surfactant decreases, showing a gradual decrease in CMC values with increasing temperature. From neutron reflection experiments on the monolayer structure of water-soluble monododecyl octaethylene glycol at the CMC value of the surfactant Penfold and coworkers observe that the thickness of the hydrophilic group decreases about 14% in the temperature range 298-323[128]. On the other hand, it has been quantitatively shown from thermodynamic considerations that micellization becomes more favorable with an increase in temperature[1]. These phenomena have been attributed to an increase in the dehydration of the head-group with interesting temperature which is in line with the observation of the present study. Micelles of ionic surfactants bind a considerable amount of counter-ions to the charged surface . At a definite temperature, the degree of

Table 3.2: **The Counter-ion binding constant (β) values at different temperatures in different medium for CTAB and TTAB.**

Surfactant	Medium	Counter-ion binding constant (β)				
		293K	**298K**	**303K**	**308K**	**313K**
CTAB	**Water**	-	0.80	0.70	0.67	0.66
	0.01M NaCl	0.84	0.82	0.80	0.75	0.69
TTAB	**Water**	0.71	0.71	0.70	0.70	-
	0.01M NaCl	0.80	0.71	0.71	0.71	-

Table 3.3: Aggregation numbers at different temperature for CTAB and TTAB.

Surfactant	Medium	Aggregation number				
		293K	**298K**	**303K**	**308K**	**313K**
CTAB	**Water**	-	28	26	23	21
	0.01M NaCl	35	84	62	60	45
TTAB	**Water**	14	12	10	9	-
	0.01M NaCl	15	24	20	17	-

ionization α, of micelles was determined from the ratio of the pre-micellar slope to the post-micellar slope[125] shown in Figures 3.7, and 3.9 for aqueous CTAB and CTAB-0.01M NaCl solution respectively. Similarly, degrees of ionization have been determined from Figures 3.8 and 3.10 for the aqueous TTAB and TTAB-0.01M NaCl respectively. The values of the degree of counter-ion binding, β obtain from the relation β= (1-α) are listed in Table 3.2. All β values were considered within a range of 1-2% error during slope selection. It is clear from Table 3.2 that β values decrease with increasing temperature. This is due to the decrease in the charge density of the micellar surface caused by the decrease in the aggregation number of the micelles with an increase in temperature. The β values are found to be significantly higher and less sensitive to temperature in the presence of NaCl than the corresponding values in pure water. But the aggregation number is very sensitive in presence of NaCl. Table 3.3 shows that in presence of NaCl the aggregation of CTAB is twice than the corresponding value of pure aqueous solution of TTAB. Table 3.3 shows that the aggregation number decreases gradually with increasing temperature. It has been reported that the presence of electrolytes favors micellization by increasing the aggregation number[110,127]and increase the hydrophobicity in micelle core**.** The increase in hydrophobic character of the surfactants decreases the CMC, induces sphere-to-rod transition at lower concentration with the addition of NaCl in surfactant solution[110]. Moreover, an increase in aggregation number increases the charge density which results in a decrease in the degree of dissociation of the micelles and gives higher β values. This is an agreement with observed lowering the CMC values of CTAB and TTAB in the presence of NaCl due to the screening of surface charge by the excess counterion.[127]

3.3 SURFACE EXCESS CONCENTRATION

Figures 3.13 and 3.14 show the variation of the surface excess concentration (Γ) of in different temperatures in water and NaCl solution for CTAB and TTAB respectively. The Γ values of CTAB and TTAB at a definite temperature was calculated from the slope of the straight line of the surface tension vs. $\log_{10}C$ plot before the CMC with help of the following equation[128].

$$\Gamma = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial lnC}\right)_{T,P} \quad \text{.....(3.1)}$$

Here, R is the gas constant ($8.314 JK^{-1}mol^{-1}$), T is the absolute temperature, C is the surfactant concentration in the bulk. All Γ values have been calculated within 1-2% error. Figure 3.13 shows the Γ values of CTAB at different temperatures in pure water and in the presence of NaCl. It is clearly seen from the figures 3.13 and 3.14 that in both cases the Γ values gradually decrease with an increase in temperature. To explain the reason we must consider firstly, the dehydration of the hydrophilic head-group and secondly, the thermal motions of the adsorbed molecules at the air-water interface. The dehydration effect results in shrinkage of the head-group size and provides a close molecular packing in the adsorbed monolayer. On the other hand, with an increase in temperature the adsorbed molecules at the air-water interface become disorganized due to an increase in kinetic energy, thermal motion and chain flaxibility[7, 8] . These opposing thermally controlled effects will help to disclose the reason of lowering of the Γ values with temperature as shown figure 3.13 & 3.14 for CTAB and TTAB respectively. As the temperature increase van der Waals interactions between the alkyl chains become more and more unfavorable. Besides, an increase in the temperature brings about perturbation in the adsorbed molecules that dominates over the dehydration effect and hinders closer molecular packing of the

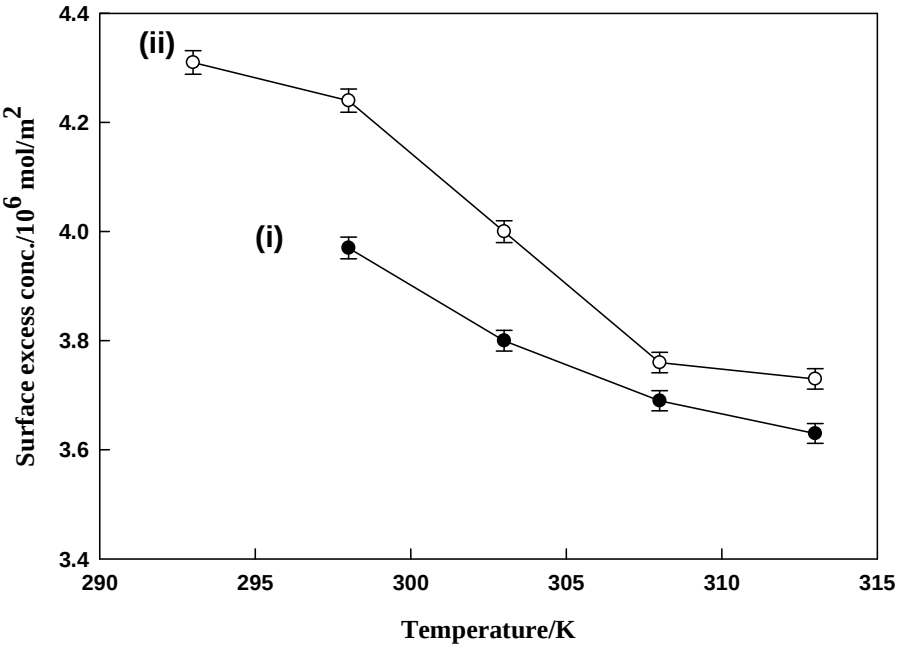


Figure 3.13: Surface excess concentration of CTAB (i) in pure and (ii) in 0.01 M aqueous solution of NaCl.

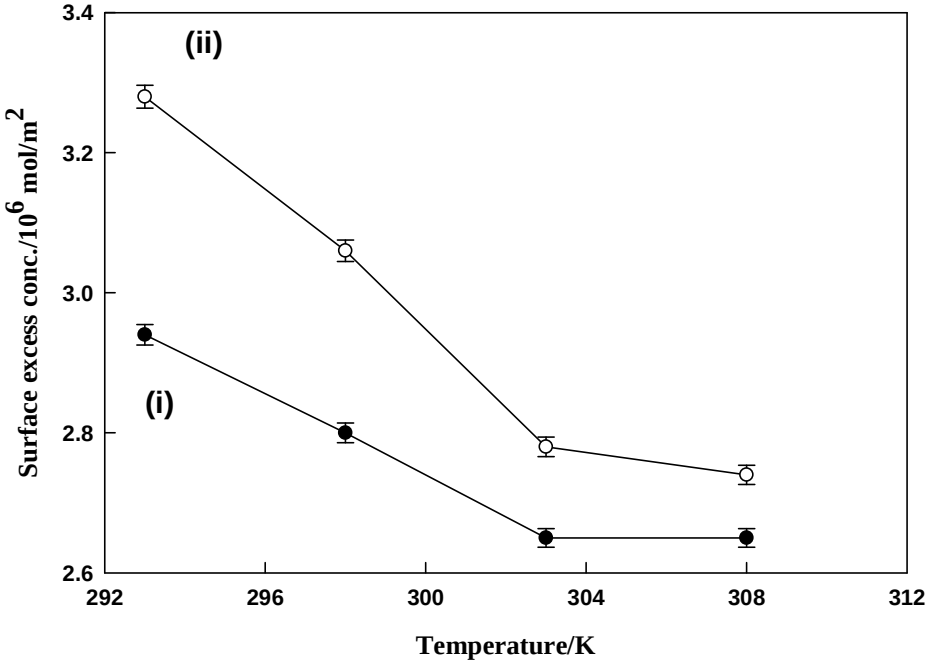


Figure 3.14: Surface excess concentration of TTAB (ii) in pure and (ii) in 0.01 M aqueous solution of NaCl.

monolayer at the air-water interface. Consequently, the Γ values show a gradual decreasing trend with increasing temperature. Besides, for solutions of ionic surfactants an electrostatic surface potential acts as a barrier for the adsorption of additional molecules as they migrate from the bulk of the solution to the air-water interface. When an electrolyte is introduced to the surfactant solution electrostatic screening of surface potential occurs at the air-water interface[129,130]. As a result, the obstruction for further adsorption of surfactant molecules is substantially reduced, giving higher surface excess concentration of the adsorbed molecules in the presence of NaCl.

3.4. THERMODYNAMICS OF BULK MICELLIZATION AND SURFACE ADSORPTION

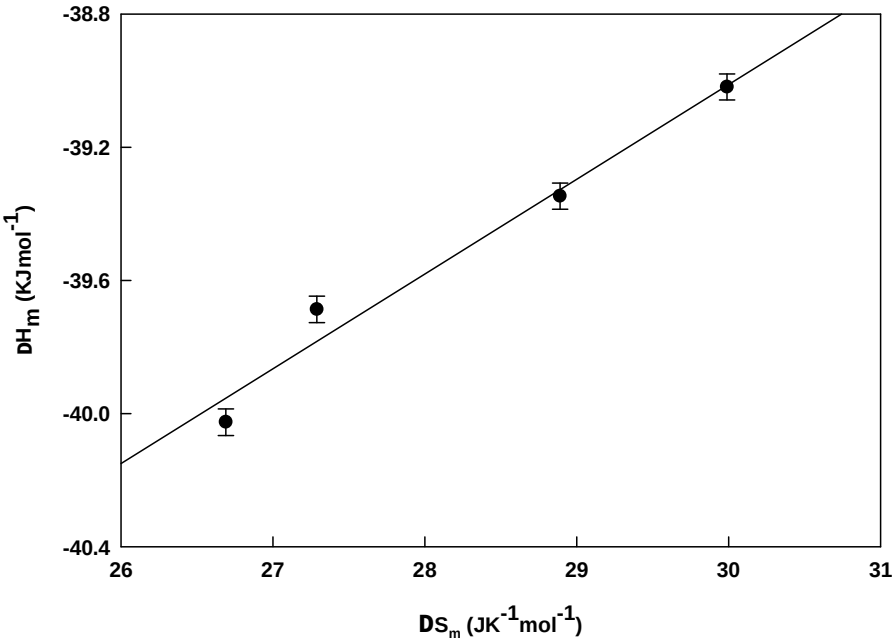
The thermodynamics of the micelle formation of both ionic and nonionic surfactants have been studied for a long time by measuring their CMC over a wide range of temperatures [4-12].The free energy (ΔG_m^o), the enthalpy (ΔH_m^o), and the entropy (ΔS_m^o), changes of micellization have been calculated from the following expression[113]:

$$\Delta G_m^o = (1 + \beta)\mathcal{R}\mathrm{T}[\ln Xcmc] \quad \textbf{(3.2)}$$

$$\Delta S_m^o = -\left\{\frac{d\Delta G_m^0}{dT}\right\} \quad \textbf{(3.3)}$$

$$\Delta H_m^o = T\Delta S_m^o + \Delta G_m^o \quad \textbf{(3.4)}$$

Where β is the degree of counter-ion binding and X_{cmc} is mole fraction of the surfactants CTAB & TTAB at the CMC. All thermodynamic parameters have been calculated within 1-2% error. The values of the free energy change ΔG_m^o for micellization of CTAB and TTAB are found to be negative. This indicates that all temperatures the transfer of methylene group of surfactants from aqueous solution to the micellar systems are



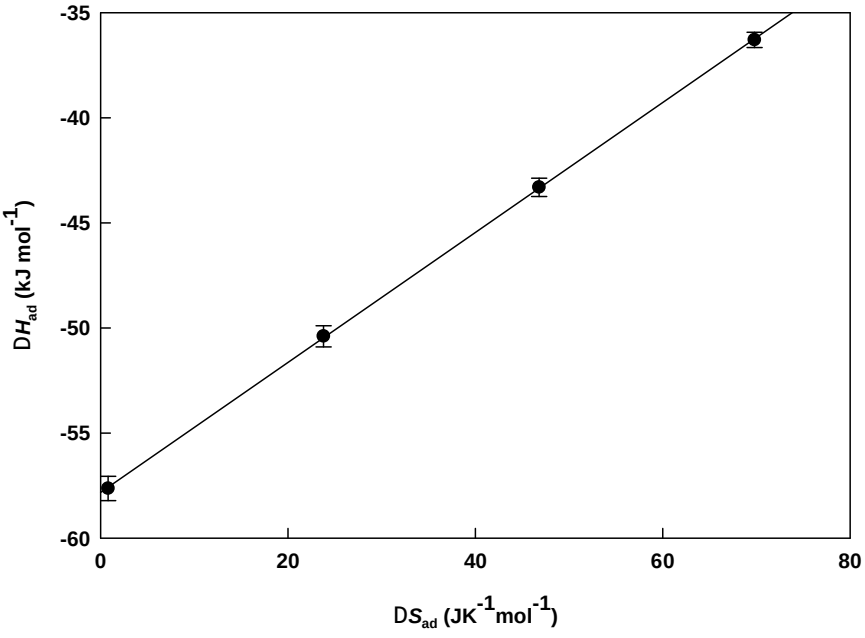


Figure 3.15: Enthalpy-Entropy compensation plot for (a) Micellization (b) Surface Adsorption of CTAB in aqueous solution

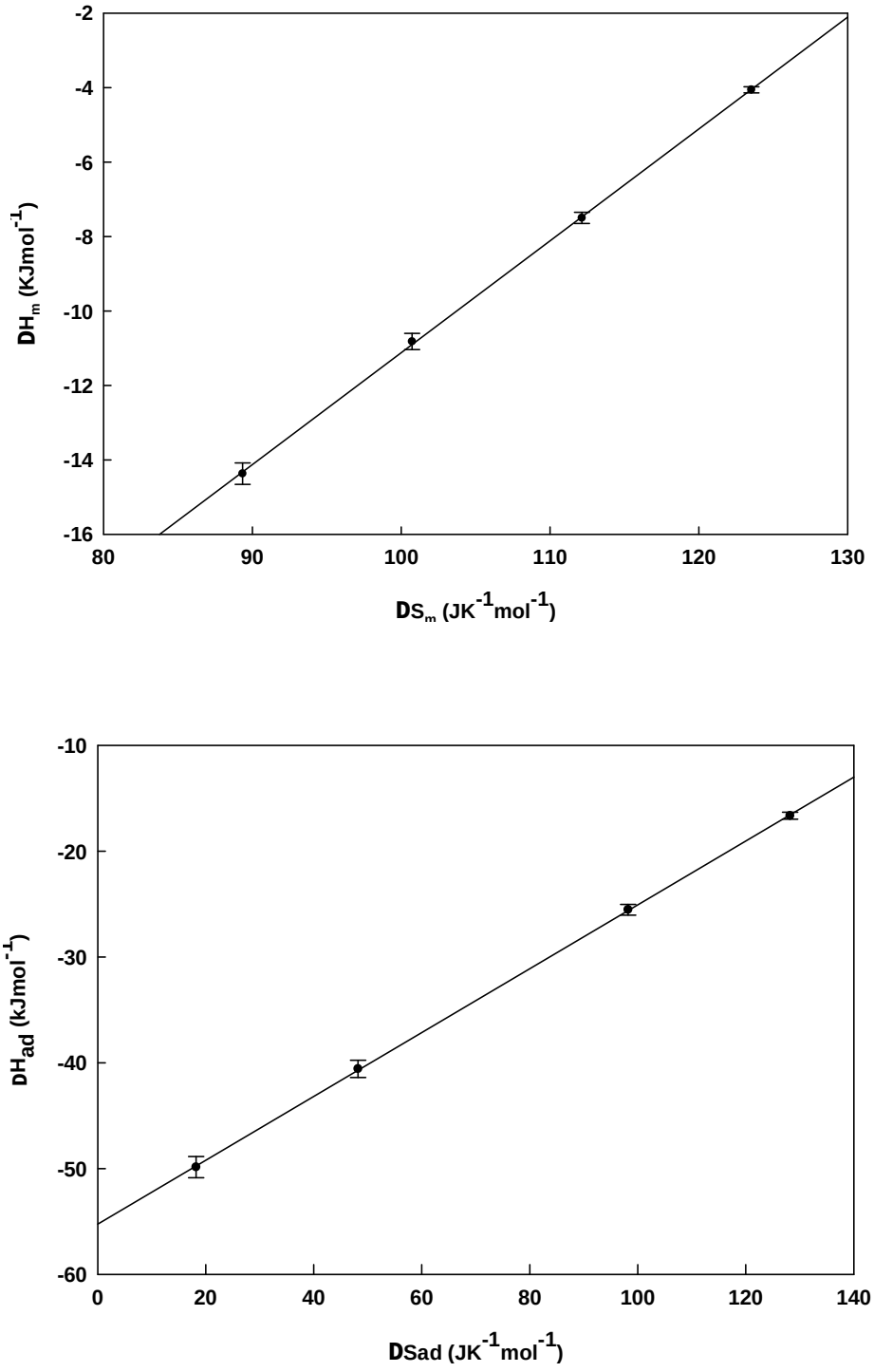


Figure 3.16: Enthalpy-entropy compensation plots for (a) micellization and (b) surface adsorption of TTAB in aqueous solution.

spontaneous process. It is evident from the table that the ΔG_m^o values of CTAB are more negative than that of TTAB. This suggests that CTAB forms micelles more spontaneously than TTAB. Generally, longer alkyl chain length results in considerably more negative values of ΔG_m^o for all type of surfactants[131, 89]**.** Usually upon micellization , the destruction of higher degree of hydrogen bonding around the alkyl chains gives a positive enthalpy change[5,7,125]. Despite, the ΔH_m^o values for micellization are found to be negative and become more negative with increasing temperature as shown in Tables 3.4 and 3.5 for CTAB and TTAB respectively. The values are found to be in good agreement with literature values [20,125]. The negative ΔH_m^o values are associated with the hydrophobic interaction between alkyl chains due to their tendency for transferring from the solvent environment to the interior of the micelle. The negative ΔH_m^o value can also occur when a substantial number of water molecules surrounding small hydrophilic head groups become more important than destruction of the iceberg around surfactant alkyl chain [7, 26]. In addition, the negative ΔH_m^o values can be taken as the evidence of London dispersion force, a major attractive force for micellization which becomes more and more dominant with increasing the hydrocarbon chain length[118]. As the temperature increases the hydrogen bond between the water molecules is diminished. Consequently, less energy is required to break up the iceberg structure around hydrophobic alkyl chains. It has been observed from the Tables 3.4 and 3.5 that all ΔH_m^o values are negative for CTAB and TTAB. With increasing the chain length of a surfactant molecule, the enthalpy of micellization becomes more negative. This suggests that the enthalpy term for CTAB is more effective in contributing to the free energy term than the TTAB. On the other hand, the ΔS_m^o values are found to be positive and the values decrease with increasing temperature. The positive ΔS_m^o values indicate that the micellization process is governed by the entropy gain associated

Table 3.4: Thermodynamic Parameters of Adsorption and Micellization* of the CTAB Surfactants.(*The cmc values were taken in mole fractions for the calculation of the thermodynamic parameters.)

Temp/ K	ΔH_m^o/ kJmol^{-1}	ΔH_{ad}^o/ kJmol^{-1}	ΔS_m^o/ Jmol^{-1}K^{-1}	ΔS_{ad}^o/ Jmol^{-1}K^{-1}	ΔG_m^o/ kJmol^{-1}	ΔG_{ad}^o/ kJmol^{-1}
298	-39.02	-36.30	29.99	69.80	-47.96	-57.10
303	-39.35	-43.31	28.89	46.80	-48.10	-57.50
308	-39.69	-50.40	27.29	23.80	-48.25	-57.73
313	-40.03	-57.64	26.69	0.80	-48.38	-57.89

Table 3.5: Thermodynamic Parameters of Adsorption and Micellization* of the TTAB Surfactants

Temp/ K	ΔH_m^o/ kJmol^{-1}	ΔH_{ad}^o/ kJmol^{-1}	ΔS_m^o/ Jmol^{-1}K^{-1}	ΔS_{ad}^o/ Jmol^{-1}K^{-1}	ΔG_m^o/ kJmol^{-1}	ΔG_{ad}^o/ kJmol^{-1}
293	-4.06	-16.65	123.53	128.20	-40.259	-54.20
298	-7.50	-25.54	112.14	98.20	-40.919	-54.80
303	-10.82	-40.58	100.74	48.20	-41.345	-55.20
308	-14.37	-49.86	89.34	18.20	-41.891	-55.50

Table 3.6: Thermodynamic Parameters of Adsorption and Micellization* of the CTAB-0.01M NaCl Surfactant solution.

Temp/ K	DGm/ kJmol^{-1}	DGad/ kJmol^{-1}	DHm/ kJmol^{-1}	DHad/ kJmol^{-1}	DSm/ Jmol^{-1}K^{-1}	DSad/ Jmol^{-1}K^{-1}
293	-46.43	-53.58	92.15	79.24	473.00	453.00
298	-43.83	-51.09	50.81	41.76	317.56	311.00
303	-40.91	-48.03	8.23	3.46	162.16	169.00
308	-42.04	-49.22	-39.96	-40.52	6.76	28.30
313	-43.34	-51.12	-89.87	-86.62	-148.64	-113.00

Table 3.7: Thermodynamic Parameters of Adsorption and Micellization* of the TTAB-0.01M NaCl Surfactant solution.

Temp/ K	DGm/ kJmol^{-1}	DGad/ kJmol^{-1}	DHm/ kJmol^{-1}	DHad/ kJmol^{-1}	DSm/ Jmol^{-1}K^{-1}	DSad/ Jmol^{-1}K^{-1}
293	-40.65	-51.38	-5.37	32.77	120.40	287.20
298	-38.90	-51.04	-28.05	-24.46	36.40	89.20
303	-38.69	-53.02	-53.11	-85.98	-47.60	-108.80
308	-37.93	-52.36	-78.46	-146.86	-131.60	-306.80

with the destruction of the iceberg around the hydrophobic alkyl chain. The decrease in ΔS_m^o values with increasing temperature suggests that disordering of water molecules become less pronounced with increasing temperature due to the destruction of the iceberg structure around the alkyl chain. On the other hand, lower values of ΔS_m^o term for CTAB compared to those of TTAB are probably a result of the organization of a greater number of CTAB molecules from randomly oriented monomers to well organized micelle structure. Tables 3.4 and 3.5 also show the thermodynamic quantities of adsorption of CTAB and TTAB at the air-water interface. The free energy of adsorption is defined as the energy required adsorbing one mole of surfactant molecules from solution to the surface at unit surface pressure. The ΔG_{ad}^o values at different temperature were calculated from the following expression[1,132].

$$\Delta G_{ad}^o = \Delta G_m^o - (\pi_{cmc}/\Gamma_{max}) \quad \textbf{(3.5)}$$

Where, $\pi_{cmc}$and Γ_{max} are the equilibrium surface pressure and the surface concentration of the adsorbed molecules, respectively, at and above the CMC value. ΔS_{ad}^o and ΔH_{ad}^o values are found to be negative over the studied temperature range indicating that the surface adsorption is spontaneous. With increasing temperature the ΔG_{ad}^o values become a bit more negative, suggesting that adsorption becomes more spontaneous with increasing temperature. These results are consistent with the increase in hydrophobicity of the CTAB and TTAB molecules caused by dehydration of the head-group with increasing temperature. At a given temperature, the ΔG_{ad}^o values of CTAB are found to be more negative than the corresponding value of TTAB (Table 3.6 and 3.7). This may due to longer hydrocarbon tail present in CTAB than that of TTAB. Moreover, at a definite temperature the ΔG_{ad}^o values are found to be more negative than the corresponding ΔG_m^ovalues, suggesting that adsorption of monomeric surfactant molecules at the air-water

interface is more spontaneous than micelle formation in the bulk. The ΔH_{ad}^{o} values are all negative, which is in line with previous observations[7,12] and become more negative with increasing temperature. At higher temperatures, the surfactant is less hydrated and requires less energy to absorb at the air-water interface. As a result, ΔH_{ad}^{o} values become more and more negative than the corresponding ΔH_{m}^{o} values at all temperatures. Moreover, ΔH_{ad}^{o} values of CTAB are more negative than the corresponding values of TTAB. This result implies stronger van der Waals interaction between alkyl chains during micellization due to the presence of longer hydrophobic chain in CTAB. The ΔS_{ad}^{o} values are found to decrease with increasing temperature. The ΔS_{ad}^{o} value is governed by the following competitive factors: A positive ΔS_{ad}^{o} values 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. On the contrary, a negative ΔS_{ad}^{o} 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 rational freedom of the adsorbed molecules at the air-water interface. Since with increasing temperature most of the iceberg structure is destroyed, the second effect progressively dominates over the first one. Consequently, ΔS_{ad}^{o} values show a gradual decreasing trend with increasing temperature. At a given temperature, the ΔS_{ad}^{o} values of TTAB are found to be more positive than the corresponding value of CTAB (Table 3.6 and 3.7). This may due to longer hydrocarbon chain present in CTAB than that of TTAB. The entropy-enthalpy compensation plots for both surface adsorption and bulk micellization for CTAB and TTAB are shown in Figures 3.15 and 3.16 respectively. An anticipated linear relationship was observed both for micelle and monolayer formation as shown in figures 3.15 (a) & 3.15(b) for CTAB and 3.16 (a) & 3.16 (b), respectively. The observed enthalpy-

entropy linear relationship can be interpreted by the equation,

$$\Delta H_{m/ads} = Tc\,\Delta S_{m/ads} + \Delta H_{m/ads} \quad \text{..... (3.6)}$$

Table 3.8 : T_c value for CTAB and TTAB in water and 0.01M NaCl solution.

Surfactants solution	Process	Compensation Temp. (T_c)
CTAB in Water	Adsorption	305K
	Micellization	294K
CTAB-0.01M NaCl	Adsorption	292K
	Micellization	293K
TTAB in Water	Adsorption	302K
	Micellization	300K
TTAB-0.01M NaCl	Adsorption	303K
	Micellization	290K

Where the intercept ($\Delta H_{m/ads}$) gives the information about the solute-solute inceraction. The enthalpy and entropy terms are found to compensate each other for both micellization and adsorption at the air-water interface and the linear relationship indicates same mechanism for all the processes. The slope of the plot, T_c having the dimension in Kelvin, is known as the compensation temperature associated with the interaction between the solute and the solvent. It has been reported that the values of compensation temperature lie in a relatively narrow range from about 250 to 315K, for all process involving aqueous

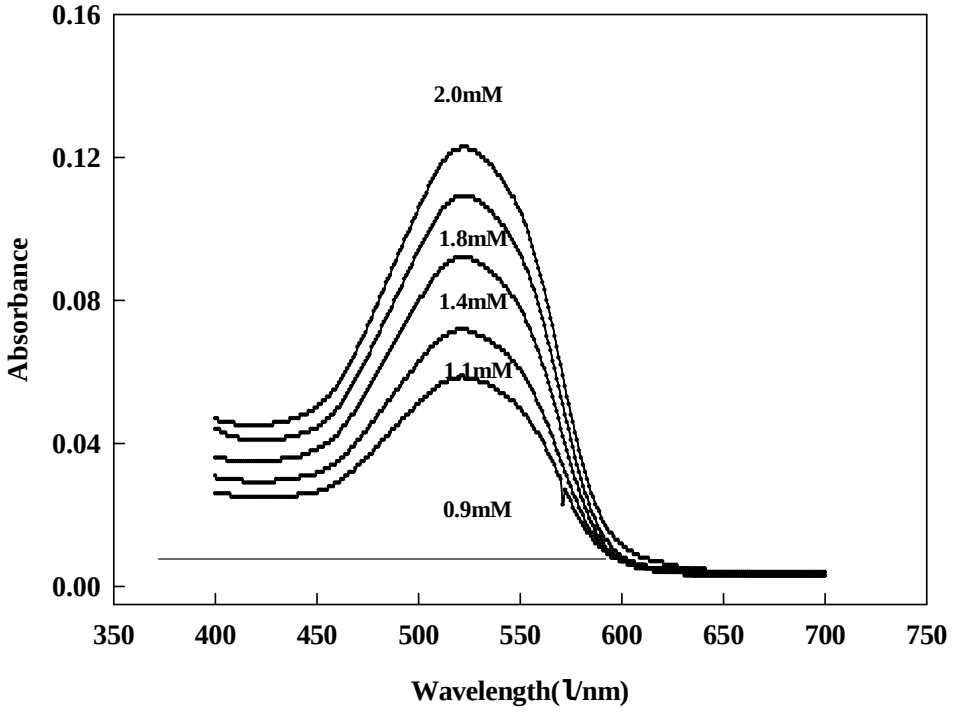


Figure 3.17: Absorbance vs. wavelength plot of aqueous CTAB solution with SUDAN RED B at different CTAB concentrations

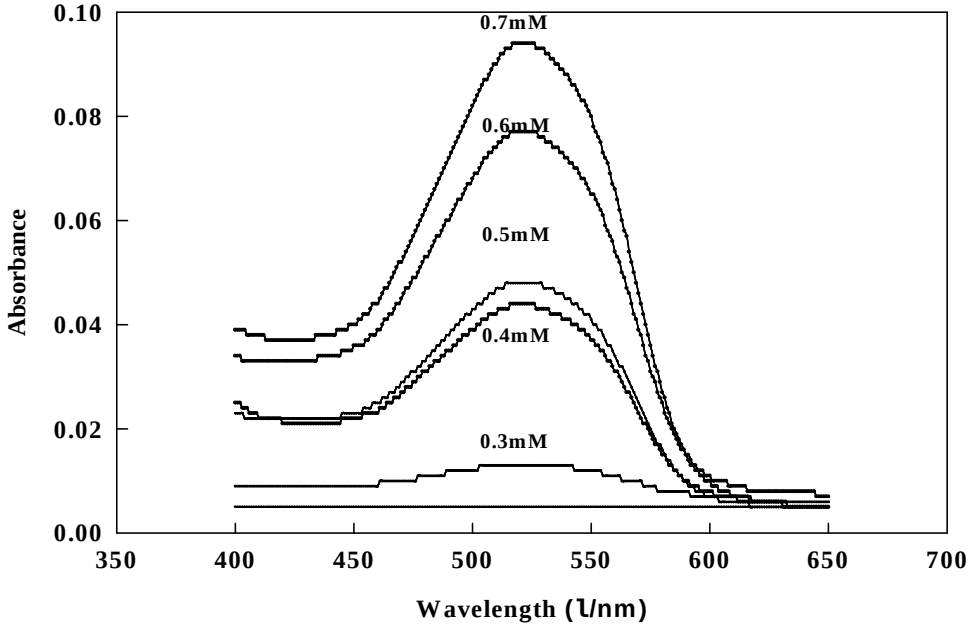


Figure 3.18: Absorbance vs. Wavelength plot of CTAB-0.01M NaCl solution for Sudan Red B at different CTAB concentrations.

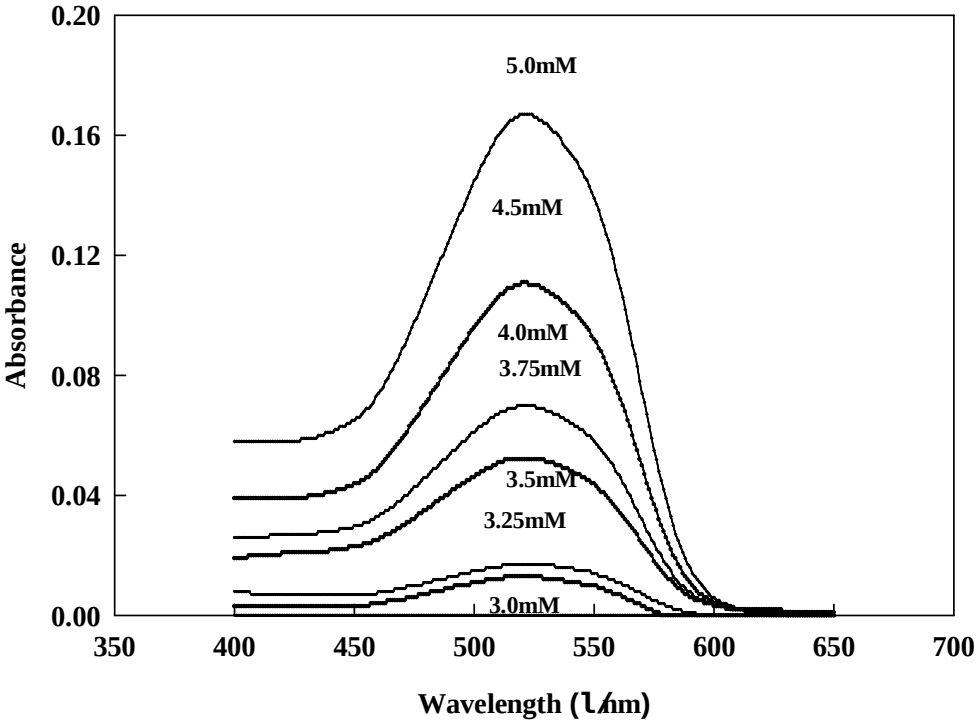


Figure 3.19: Absorbance vs. Wavelength plot of aqueous TTAB with SUDAN RED B at different TTAB concentrations.

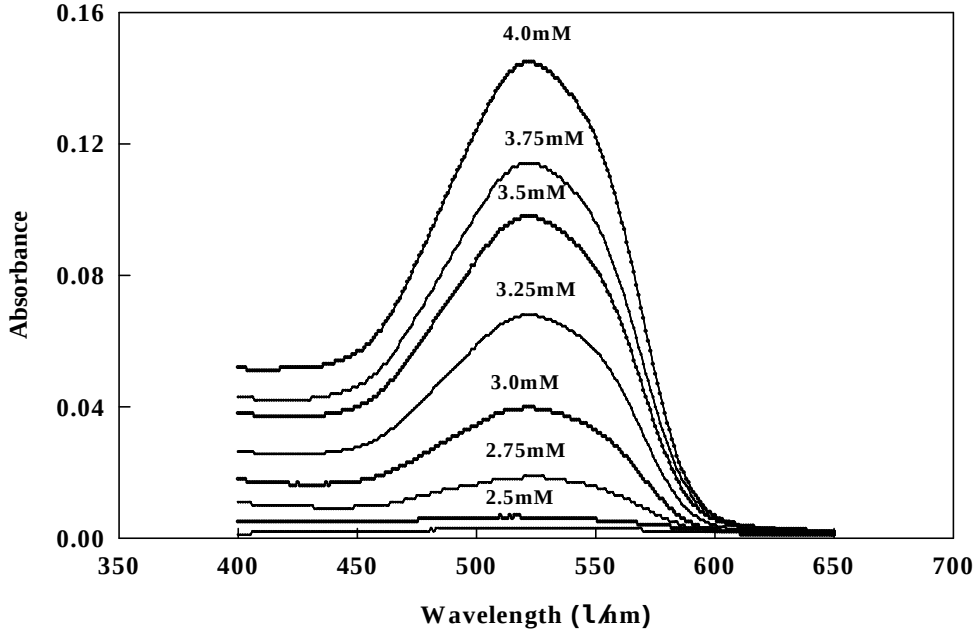


Figure 3.20: Absorbance vs. Wavelength of TTAB-0.01M NaCl with SRB at different temperatures

solution of small molecules and physiological processes[133]. The T_c values obtained from the slopes of figures 3.15 & 3.16 are shown in Table 3.8. The values obtain for CTAB and TTAB for both adsorption and micelle formation are found to lie in the suggested literature values[29,134,135] . When the entropy contributes less to the free energy, its counterpart, the enthalpy term contributes more to keep the negative free energy change to a nearly constant value. Such a behavior has been observed for aqueous solution of ionic surfactant previously [29,134,135].

3.5 SOLUBILIZATION STUDY OF SUDAN RED B

Solubilization is one of the most important properties of surfactant which occurs upon formation of micelles. The solubilization of SBR studied in both pure aqueous and aqueous NaCl systems are shown in Figures 3.17 & 3.18 for CTAB and 3.19 & 3.20 for TTAB. The solubilization of SRB was carried out at several surfactant concentrations ranging from 0.3 to 2.0 mM for CTAB and from 2.0 to 5.0 mM for TTAB with a fixed amount of SRB to ensure solubilization equilibrium with the dye in micelles. The hydrophobic effect is accompanied by a bathochromic shift due to solubilization of SRB in CTAB and TTAB micelles. It is well known that the features of electronic spectra are related to polarity of the medium. As the SRB molecules are solubilized in the micelles a gradual shift to the red was observed. After solubilization of SRB the λ_{max} values was found to be 518 nm (at the CMC value in pure water and aqueous NaCl solution) that reached a maximum 522 nm for 2.0 mM CTAB in pure water and 521 nm for 0.7 mM CTAB in 0.05M NaCl solution. On the other hand, after solubilization of SRB the λ_{max} was found 521nm for all the concentration of TTAB in pure water and in NaCl solution 518 nm at 2.25 mM of TTAB and 521 nm at 4.0 mM of TTAB. It is important to note here that

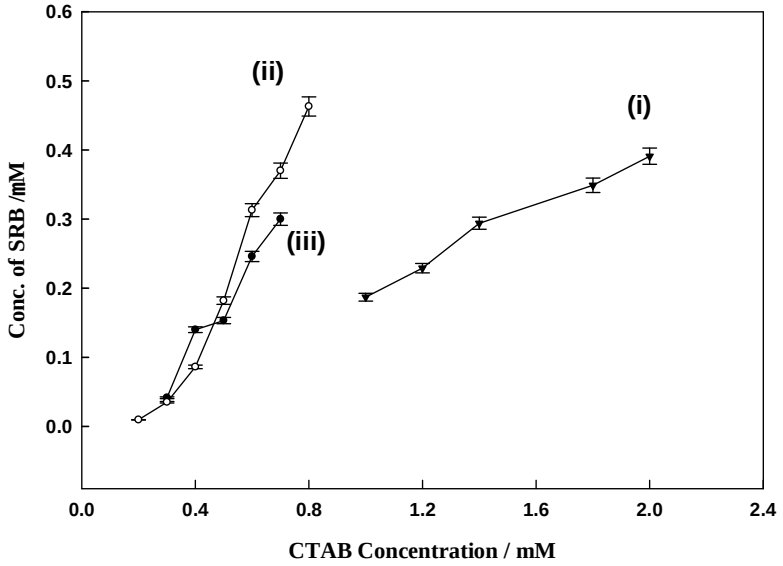


Figure 3.21: Solubilization of Sudan red B in CTAB solution in (i) pure water, (ii) 0.05 M aqueous NaCl solution and (iii) 0.01M aqueous NaCl solution.

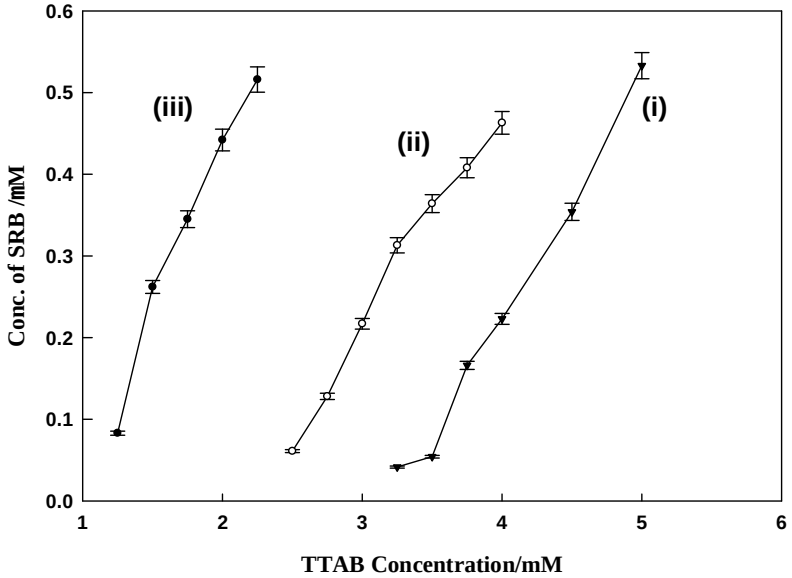


Figure 3.22: Solubilization power of Sudan red B in TTAB solution in (i) pure water, (ii) 0.01 M aqueous NaCl solution and (iii) 0.05M aqueous NaCl solution.

below the CMC no absorbance was observed indicating that SRB is insoluble in both CTAB and TTAB solutions when their concentration is below the CMC. This implies that due to the lack of hydrocarbon like environment of the miceller core, SRB is insoluble in the CTAB and TTAB solutions when the concentration is below their respective CMC value. It has been reported that the molecules solubilized in the outer portion of the micelle core are capable of reducing CMC values of surfactant[136]. In the present work it was observed that SRB has no significant influence on the CMC values in pure water and in aqueous NaCl solution. Therefore the red shift indicates that SRB is solubilized in the oil like environment of the micellar core. This micellar core has a liquid like structure with low dielectric constant[137].Thus, hydrophobic compounds are mixed and solubilized readily in this environment and entangles with the alkyl chains of the surfactants. It has been reported that dye molecules interact with the micellar aggregates through the attraction of the π electrons of the aromatic ring to the cationic head group of the surfactant on the micellar surface[137,]. The solubilized molecules are thereby incorporated into palisade layer of the micelle which results in a red shift in the UV-visible spectrum. Due to the presence of the counter-ion the potential at the micelle surface greatly reduced. It has reported that the presence counter-ion imparts an increase in the aggregation number of the micelle[138,139]. Consequently, the soubilization capacity increases significantly in the presence of the counter-ion. This occurs due to the reduction in the electrostatic repulsions between the charged head-groups of the surfactant in the presence of the counter-ion[10,139] and result in a decrease in the surface area of head-group as well as the CMC value. The solubilization of SRB in the micellar system in NaCl solution also starts at lower surfactant concentration than in pure water. The solubilizing power increases linearly as a function of CTAB and TTAB concentration in pure water and in the presence of NaCl. The molar

solubilization ratio (MSR) of SRB in CTAB and TTAB are shown in Tables 3.9 and 3.10. It is clear from the Tables 3.9 and 3.10 that MSR values increase with increasing salt concentration. It clearly suggests that the presence of salt increase the miceller aggregation number of the surfactants. MSR values of CTAB are found to be higher than the corresponding values of TTAB except for the value of CTAB in pure water. This is probably due to the longer hydrocarbon chain of CTAB. In all these cases, the CMC does not vary upon solubilization only when CTAB and TTAB forms oil-like environment of micellar core at and above CMC. Below the CMC solubilization does not occur due to the absence of favorable oil-like environment of the micelle core.

Table 3.9: Molar Solubilization Ratio (MSR) values of SRB in CTAB

Surfactant	NaCl Concentration (M)	Regression coefficient(R^2)	MSR
CTAB	0.00	0.982	2.0×10^{-3}
CTAB	0.01	0.98	5.72×10^{-3}
	0.05	0.987	9.41×10^{-3}

Table 3.10: Molar Solubilization Ratio (MSR) values of SRB in TTAB

Surfactant	NaCl Concentration (M)	Regression coefficient(R^2)	MSR
TTAB	0.00	0.9823	2.733×10^{-3}
TTAB	0.01	0.986	2.872×10^{-3}
	0.05	0.97	4.184×10^{-3}

CONCLUSION

In the present work, we have investigated the surface adsorption and bulk micellization of two cationic surfactants namely cetyletrimethylammonium bromide (CTAB) and tetradecyltrimethylammonium bromide (TTAB) in pure water and aqueous NaCl solution. Since micellization occurs only after the krafft temperature of the surfactant, the T_k values of the surfactants were also measured in pure water and aqueous NaCl solution. The T_k values of CTAB and TTAB in pure water were found to be 24.8^{o}C and 12^{o}C respectively. It is interesting to note here that for both the surfactants, the T_k values in presence of NaCl decrease with increasing concentration of the electrolyte. In aqueous media, the CMC values are found to increase slightly with increasing temperature. On the other hand, the CMC values of CTAB and TTAB in presence of NaCl were found to increase and then decrease showing a maximum at 27^{o}C and 30^{o}C respectively. It should be noted that the CMC values of CTAB and TTAB in presence of NaCl are much lower than the corresponding values in pure water. The values of surface excess concentration (Γ_{max}) are found to decrease gradually with increasing temperature which can attributed to an increase in thermal motion and chain flexibility of the adsorbed molecules at the solution surface. The ΔG_{ad}^o values are found to be more negative than the corresponding ΔG_m^o values, suggesting that the adsorption of CTAB and TTAB at the air-water interface is more favorable than their micellization in the bulk. The increase in negative value of ΔH_m^o and decrease in positive ΔS_m^o values indicate that solvophobic contribution decreases while the London dispersion force between the alkyl chains increases with the rise of temperature. The ΔS_{ad}^o values decrease with increasing temperature, which indicates that the disordering of the ice-berg structure around the alkyl chains becomes less pronounced

with increasing the concentration of NaCl. The solubilization of water-insoluble SRB in the micellar environment of the surfactants has also been investigated. SRB being hydrophobic in nature interacts with the hydrophobic micellar core and becomes solubilized in the oil-like environment of the micelles. The extent of solubilization increased with increasing the concentration of the surfactants. This is due to the increase in the number of micelles in the bulk of the surfactant solution. In presence of NaCl, the hydrophobic interaction increase by reducing the surface potential of the micelles and increase the aggregation number result increase the oil-like environment of the micelle core. This helps to solubilize more SRB compared to that in aqueous CTAB and TTAB solutions in pure water. A red shift occurs when SRB solubilization occur in the oil-like micelle core. Those values indicate that the SRB has solubilized in the oil-like environment of the micelle core.

Surfactants have a wide verity of industrial applications. They are also used in household cleaning products, cosmetics, pharmaceuticals, mining and ore flotation, paints and coatings. Application of surfactants lies in their capacity of micelle formation. In this regard Krafft temperature is an important phenomenon. Because below the Krafft temperature surfactants lose many of their characteristic properties such as dispersing, emulsifying, wetting, micelle forming, solubilizing, de-foaming etc. In the present work, it has been observed that both T_K and CMC values of the surfactants decrease in the presence of NaCl. Therefore, depressed T_K and lower CMC values of the surfactants in the presence of NaCl will pave the way for their wider industrial applications.

1. Mayers, D. ; *Surfactant Science and Technology,* 3rd edition, John Wiley & Sons, Inc.Publication, **2006.**

2. Martin, P-R., Prieto,G.; Rega, C.; Varela L. M.; Sarmiento, F.; Mosquera, V.; *Langmuir* **1998**, 14, 4422

3. Chakraborty, T.; Ghosh, S. Moulik S.P.; *J. Phys. Chem. B* **2005**, 109, 14813

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

5. Zheng, O. Zhao; *J. Colloid and Interf. Sci.***2006**, 300, 749

6. Farias, T; Menorval, L. C.; Rivera, A.; *Colloids and Surf. A***2009**, 345, 51

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

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

9. Metha,S.K.; Bhasin,K.K.; Chauhan,R.; Dham, S.; *Colloids and Surfaces A* **2005**, 255, 153.

10. Kim, J.H.; Domach, M.M., Tilton R. D.; *Langmuir* **2000**, 16, 10037-10043

11. Liu, C.; Desai, K. G. H.; Liu, C.; *J. Chem. Eng. Data***2004**,49, 1847-1850

12. Aguiar, J.; Molina-B.J.A.; Peula-G.J.M. Ruiz, C.C.; *J Colloids Interf. Sci.* **2002**, 255, 382.

13. Metha, S.K.; Bhasin, K.K.; Chauhan, R.; Dham, S.; *Colloids and Surfaces A,* **2005** 235, 153

14. Nayyar, S.P.; Sabatini, D. A.; harwell, J.H.; *Environ. Sci. Tech*. **1994**, 28, 1874

15. Choucair, A.; Eisenberg, A.; *J. Am. Chem. Soc*. **2003**, 125, 11993-12000

16. Liu, C.; Desai, K. G. H.; Liu, C.; *J. Chem. Eng. Data***2004**,49, 1847-1850

17. Paria, S.; Yust, P.K.; *Ind. Eng. Chem. Res.***2006**, 45, 3558.

18. Tanford, C.; *The hydrophobic effect* (John Wiley, New York, **1973**)

19. Tanford, C.; *Proc. Nat Acad. Sci.* **1974**,71, 1811.

20. Debye, P.; *J. Phys. Chem.***1949**, 53,1.

21. Debye, P.; Ann. N.Y.; *Acad. Sci.* **1949**, 51, 573.

22. Hill,T.L.; *Thermodynamics of small system*, **1964**, Vol. 1 and 2 (Benzamin , Newyork,)

23. Hall, D.G. and Pethica, B.A.; *Nonionic surfactants, ed*. M.J. Schick (Marcel Dekker, New York, **1967**), Chap, 67

24 Franks, F.; *water a comprehensive treatise*, ed, F. Franks, Plenum Press, New York **1973**, 2, 1.

25. Narten, A.H. ; and Levy, H.A. ; *Plenum Press*, New York **1973**, 1, 311

26. Zeidler, M.D. ; *Plenum Press*, New York **1973**, 2, 529.

27. Devidson, D.W. ; *Plenum Press*, New York **1973**, 2, 115.

28. Clifford, J. , and Pethica, B.A. ; *Trans. Faraday Soc.***1965**,61, 182

29. Lindman, B. , and Brun, B.; *J. Colloid Interface Sci.***1973**,42, 388

30. Hinton, J.F. and Amis, E.S. ; *Chem. Rev.***1971**,71, 627.

31. Mukerjee, P. ; *J. Colloid Sci.***1964**, 19, 722.

32. Ekwall, P. and Holmberg, P,; *Acta. Chem. Scand*. **1965**,19, 455.

33. Courchene, W.L. ; *J. Phys. Chem.***1964,**68, 1870.

34. Tokiwa, F. and Ohki, K. ; *J.Phys. Chem.***1967,**71, 1343.

35. Corkill, J.M.; Goodman, J.F. and Walker, T. ; *Trans Faraday Soc.***1967**,63, 768.

36. Stigter, D. ; *J. Phys. Chem.***1974**,78, 2480.

37. Elworthy, P.H., and Macfarlane, C.B.; *J. Phys. Soc.***1963**, 907

38. Elworthy, P.H., and McDonald, C. ; *Kolloid-Z.Z.Polm*. **1964**,195, 16.

39. Elworthy, P.H. , and Macfarlane, C.B.; *J. Chem. Soc*. **1964**, 311.

40. Johansson, A. and Drakenberg, T. ; *Mol. Cryst. Liquid Cryst*. **1971**,14, 23.

41. Lindblom, G. , Persson, N.O. , Lindman, B. and Arvidson, G. , Bunsenges, Ber. ; *Phys. Chem*. **1974**, 78, 955.

42. Persson, N.O. and Lindman, B. ; *J. Phys. Chem.***1975**, 79, 73.

43. Clifford, J. and Pethica, B.A.; *Trans. Faraday Soc.***1964**, 60, 1483.

44. Podo, F.; Ray, A. and Nemethy, G.; *J.Am. Chem. Soc*.**1973**, 95, 6164.

45. Clemett, C.J.; *J. Chem.Soc. A*, **1970**, 22, 51

46. Corkill, J.M.; Goodman, J.F. and Wyer, J.; *Trans Faraday Soc.***1969**, 65, 9.

47. Andrasko, J. and Foresen, S.; *Biochem. Biophys. Res. Commun*. **1974**,60, 813.

48. kamenka, N.; Fabre, H.; Charro, M. and Lindman, B.; *Acad. Sci. Paris***1975**, 281, 1045

49. Pártay, L.B.; Sega, M.; Jedlovszky, P.; *Langmuir*.**2008**, 24, 19

50. Arp, H. P. H. and Goss, K.; *Environ. Sci. Technol.*, **2009**, *43* (22), 8542–8547

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

52. Emerson, M.F. and Holtzer, A.; *J. Phys. Chem.***1967**,71, 1898.

53. Larsen, J.W. and Magid, L.J.; *J. Am. Chem. Soc.***1974**,96, 5774.

54. Reiss-Husson, F. and Luzzati, V. ; *J. Phys. Chem***1964**, 68, 3504.

55. Lindblom, G.; Lindman, B. and Mandell, L.; *J. Colloid Interface Sci*. **1973**, 42, 400.

56. Gravsholt, G.; *J. Colloid Interface Sci*. **1976**, 57, 575.

57. Ulmius, J.; Lindman, B.; Lindblom, G. and Drakenberg, T.; *J. Colloid Interface Sci.***1978**, 65, 88.

58. Ekwall, P.; *Advances in liquid crystals*, ed. G. Brown, Academic Press, New-York, **1975**, 1, 1.

59. Mukherjee, P. and Mysels, K.J. ; Critical micelle concentrations of aqueous surfactant systems, NSRDS-NBS-36, U.S. *Government Printing Office*, Washington, D.C.**1971**, 20402,

60. Mukerjee, P. and Ray, A.; *J. Phys.Chem*. **1966**,70, 2150.

61. Mukerjee, P. and Ray, A.; *J. Phys.Chem*. **1966**, 70, 2138.

62. Mukerjee, P. and Ray, A.; *J. Phys.Chem.***1966**, 79, 2144.

63. Anacker, E.K. and Ghose, H.M.; *J. Am. Chem. Soc.***1968**, 90, 3161.

64. Hoffman, H.; Nagel, R.; Platz, G. and Ulbricht, W.; *Solubilization and Microemulsion***,** 1, 263

65. Mukerjee, P.; *J. Colloid Sci*. **1962**, 66, 943.

66. Lindman, B. and Ekwall, P.; *Mol. Cryst. Liquid Cryst.***1968**,5, 79.

67. Stigter, D.; *J. Phys. Chem.***1964**, 68, 3603.

68. Mukerjee, P.; Cardinal, J.R. and Desai, N.R.; *Solubilization and Microemulsion***,** **1977**, 1, 241.

69. Stigter, D.; *J. Phys. Chem*. **1975**,79,1008.

70. Stigter, D.; *J. Phys. Chem*. **1975**, 79, 1015.

71. Stigter, D.; *J. Phys. Chem.***1974**,78, 2480.

72. Oosawa, F.; *Polyelectrolytes*, Marcel Dekker, New York, **1971**

73. Clint, J.H.; *Surfactant Aggregation*, Blackie & Son Ltd: Bishopbriggs, **1992**, 148.

74. Rosen, M. J.; *Surfactants and Interfacial Phenomena*, 3rd. ed., John Wiley & Sons, Hoboken, **2004**, 214.

75. Rosenholm, J.B.; Drakenberg, T. and Lindman, B.; *J. Colloid Interface Sci*. **1978**, 63, 538

76. Waggoner, A.S.; Keith, A.D. and Griffith, O.H.; *J. Phys. Chem*. **1968**,72, 4129.

77. Shinitzsky, M.; Dianoux, A.C.; Gitler, C. and Weber, G.; *Biochemistry***1971**,10 , 2106.

78. Hill, T.L.; *Thermodynamics of small systems*, vol. 1 and 2 (Benjamin, New York, **1964**)

79. Hall, D.G. and Pethica, B.A.; *Nonionic surfactants, ed*. M.J. Schick (Marcel Dekker, New York, **1967**), Chap, 67.

80. Hall, D.G.; *Trans, Faraday Soc.***1970**, 66,1351.

81. Hall, D.G.; *Trans, Faraday Soc.***1970**, 66,1359.

82. Hall, D.G.; *Kolloid-Z. Z. Polym.***1971**, 246, 688.

83. Mukerjee, P.; *J. Pharm. Sci.***1971**, 60, 1531.

84. Fendler, J.H. and Fendler, E.J.; *Catalysis in Micellar and Macromolecular System* (Academic Press, New York, **1975**)

85. Eriksson, J.C. and Gillberg, G.; *Acta Chem. Scand.***1966**, 20, 2019.

86. Mukerjee, P.; *J. Pharm. Sci.***1971**, 60, 1528.

87. Rhodes, C.T. and Donbrow, M.; *J. Pharm. Sci,***1965**, 54, 1059,

88.Tokiwa, F. and Aigami, K.; *Kolloid-Z. Z. Polym.***1971**, 246, 688.

89. Rehfeld, S.J.; *J. Phys. Chem.***1970**, 74, 117.

90. Rehfeld, S.J.; *J. Phys. Chem*. **1971,** 75, 3905,

91. Fendler, J.H. and Pattersson, L.K.; *J. Phys. Chem*,**1971**, 75, 3907.

92.Thomas, J.K.; *Acc. Chem. Res*. **1977**, 10, 133.

93. Ulmius, J. ; Lindblom, B. and Drakenberg, T.; *J. Colloid Interface Sci.***1978**, 65, 88.

94. Mukerjee, P.; Cardinal, J.R. and Desai, N.R. ; *Solubilization and Microemulsion.* **1977**, 1, 241.

95. Klevens, H.B.; *Chem. Rev*. **1950**, 47, 1.

96. Swarbrick, J.; Galonia, J. and Bates, T.R.; *J. Colloid Interface Sci.***1972**, 41, 609.

97. Jacobs, P.T.; Geer, R.D. and E.W. Anacker, *J. Colloid Interface Sci.***1972**, 39, 611.

98. Hartly, G.S.; *J. Chem. Soc.* **1968**, 1938

99. Samis, C.S. and Hartley, G.S.; *Trans. Faraday Soc.* 1938, 34, 1288,

100. Larsen, J.W. and Magid, L.J.; *J. Phys. Chem,***1974**,78, 834.

101. Franks, F. (ed.); *Water*, a comprehensive treatise (Plenum Press, New York, **1972-1975**)

102.Meso, C. L.; Ranieri, G.A.; Terenizi, M.; *Thermochim. Acta***1988**, 137, 143

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

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

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

106.Hirata, H.; Ohira, A.; limura, N.; *Langmuir***1996**, 12, 6044.

107.Vautier-Giongo, C.; Bales, B. L.; *J phys. Chem. B***2003**, 107, 5398

108.Davey, T.W.; Ducker, W.A.; Hayman, A.R.; Simpon, J.; *Langmuir*, **1998**,14,3210

109.Mukharjee, P.; Mysels, K. J. Kapauan, P.; *J. Phys. Chem.***1977**, 71, 4166

110.Varade, D.; Joshi, T.; Aswal, V. K.; Goyal, P. S.; Hassan, P. A.; Bahadur, P.; *Colloids Surf. A.* **2005**, 259, 95

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

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

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

114. Nishikido, N.; Matuura, R.; *Bulletin of Japan Chem. Soc.***1977**, 30, 1690

115.Vautier-Giongo C.; Bales B. L.; *J. Phy. Chem. B.* **2003**, 107, 5398-5403

116. Hassan, P. A.; Glenn, K.; Doiron, M.; Palepu, M. R.; Sharma, K. S.; Patil, S.R.; Rakshit, A. K.; *J. Phys. Chem. B.* **2004,** *108,* 12804-12812

117. Collins, K.D. ; *Bio phys.Chem*. **2012,** 167, 43

118. Zhang, L.; Somasundaran, P.; Maltesh, C.; *Langmuir* **1996,** 12, 2371

119. Heyda, J.; Lund, M.; Oncak, M,; Slavicek, P.; Jungwirth, P.; *J. Phys. Chem***. 2010,** 114, 10843

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

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

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

123. Chen, Z.; Yang, T.; Kataoka, S.; Cremer, P.S.; *J. Am. Chem. Soc.***2007**, 129, 12272

124. Nishikido, N.; Matuura, R.; *Bulletin of Japan Chem. Soc.***1977**, 30, 1690.

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

126. Mata, J.; Varade, D.; Bahadur, P.; *Thermochem. Acta.* **2005**, 428, 147

127. Beyer, K.; Leine, D.; Blume, A.; *Colloids and Surfaces B: Bio interfaces* **2006**, 49,31–39.

128**.** Rusdi, M.; Moroi, Y.; Hlaing, T.; Matsuoka, K.,; *Bull. Chem. Soc. Jpn.*, **2005**, 78, 604–610

129. Chotipong A.; Scamehorn, J. F.; Rirksomboon, T.;Chavadej, S.; Supaphol, P.; *Colloids and Surfaces A: Physicochem. Eng*. **2007**, 297, 163–171

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

131. Perger, T. M.; Rogac, M. B., *J. of Colloid and Interface Science,***2007,** 313, 288-295.

132. Dahanaayake, M.; Cohen, A. W.; Rosen, M. J.; *J. Phys. Chem*. **1982,** 90, 2418

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

134.Sugihara, G.; Hisatomi, M.; *J. Colloidal Interf. Sci.***1999**, 219, 31

135. Kabir-ud-Din, Koya, A. P.; Khan, Z. A.; *J. Colloidal Interf. Sci.***2010**, 342, 340

136. Shah, S. S.; Awan, M. A.; Ashraf, M.; Idris, S. A.; *Colloids Surf. A***1995**, 105, 319

137. Sabate, R.; Gallardo, M.; Maza, A. D. L.; Estelrich, J.; *Langmuir***2001**, 17, 6433

138. Fujio, K.; Mitsui, T Kurumizawa, H.; Tanaka, Y.; Uzu, Y.;*Colloid Polym. Sci.* **2004**,282,223

139. Schott. H.; J. *Phys. Chem.***1977**, 71, 3511.

DATA OF TTAB

Table 1: Plot of conductance vs. concentration of aqueous TTAB solution at different temperatures. (293K; 298K; 303K; 308K)

Concentration/mM	293K	298K	303K	308K
0.294	24.6	28.1	28.9	28.6
0.577	49.3	53.2	53.6	54.9
0.7549	65.2	68.5	69.8	70.9
1.019	88	89.9	90.8	92
1.38	117	121.4	120.4	120.8
1.62	141	141.2	142.3	140.6
1.88	161.4	160.2	162.4	160.4
2.106	180.6	180.3	181.6	179.1
2.325	198	199.6	200	197.8
2.536	216	214	217	214
2.74	229	227	232	230
2.938	246	243	247	250
3.129	263	257	266	263
3.363	279	274	284	280
3.542	289	285	296	297
3.716	298	298	304	308
3.884	304	305	312	319
4.047	311	310	321	326
4.264	315	316	327	332
4.417	320	320	331	338
4.566	324	324	335	342
4.711	327	328	339	346
4.852	331	330	341	350
4.989	334	334	344	354
5.122	338	-	-	357

Table 2 : Surface tension versus logarithm of the concentrations of aqueous solutions of TTAB at different temperatures. (293K; 298K; 303K;308K)

concentration (mM)	log (C)	Surface Tension (mN/m)			
		293K	**298K**	**303K**	**308K**
0.9549	-3.02	50	52.2	53.5	54.8
1.62	-2.79	42.6	44.9	46.6	47.6
2.325	-2.634	37.3	40	41.8	42.5
2.938	-2.53	33.7	36.6	38.6	39.2
3.363	-2.47	31.9	34.6	36.6	37.3
3.542	-2.45	31.4	34	36	36.7
3.716	-2.4299	31.4	33.2	35.5	36.2
4.0417	-2.39	31.3	33	35.3	36
4.417	-2.355	31.3	33	35.3	36
4.852	-2.314	31.2	33	35.3	36
4.989	-2.3	31.2	33	35.3	36
5.122	-2.29	31.2	33	35.3	36

Table 3: TTAB-0.01M NaCl conductance data at different temperature

Concentration (mM)	Conductance ($\mu S/cm$)			
	293K	**298K**	**303K**	**308K**
0.294	1062	1063	1045	1053
0.577	1086	1090	1066	1072
0.7549	1102	1106	1080	1092
1.019	1124	1130	1102	1114
1.38	1154	1159	1130	1142
1.62	1176	1181	1150	1166
1.88	1198	1202	1170	1185
2.106	1216	1222	1188	1204
2.325	1234	1239	1207	1220
2.536	1247	1253	1225	1235
2.74	1256	1264	1238	1248
2.938	1263	1272	1247	1255
3.129	1270	1280	1252	1262
3.363	1274	1286	1260	1268
3.542	1277	1291	1263	1272
3.716	1279	1296	1267	1276
3.884	1281	1300	1270	1280
4.047	1283	1304	1273	1284

Table 4: TTAB-0.01M NaCl concentration vs. surface tension data

Concentration(mM)	Log C	Conductance ($\mu S/cm$)			
		293K	298K	303K	308K
0.2940	-3.5320	62.1000	61.3000	60.6000	60.2000
0.5770	-3.2390	54.0000	52.8000	51.1000	50.0000
0.9549	-3.0200	48.0000	46.4000	44.3000	43.5000
1.3800	-2.8600	44.0000	42.1000	39.8000	38.6000
1.6200	-2.7900	42.0000	40.1000	37.6000	36.8000
2.3250	-2.6340	37.6000	35.6000	32.8000	32.6000
2.9380	-2.5300	36.8000	34.8000	32.0000	32.5000
3.3630	-2.4700	36.8000	34.8000	32.0000	32.5000
3.5420	-2.4500	36.8000	34.8000	32.0000	32.5000
3.7160	-2.4299	36.8000	34.8000	32.0000	32.5000
4.0417	-2.3900	36.8000	34.8000	32.0000	32.5000

Table 5: Dependence of CMC values of ($_i$) pure TTAB (ii) TTAB-0.01M NaCl on different Temperatures.

Temperature/K	CMC of Pure TTAB(mM)	CMC of TTAB-0.01M NaCl(mM)	CMC of TTAB-0.005M NaCl(mM)
293	3.4	2.64	2.925
298	3.7	2.72	2.934
303	3.8	2.90	2.985
308	3.82	2.72	2.972

Table 6: Temperature dependence counter-ion binding parameter, molecular crosses sectional area and Surface Excess Concentration.

T/K	Counter-ion binding (β)		A_{min}/nm^2		Surface Excess Concentration(Γ)/10^{-6}	
	Pure TTAB	TTAB-0.01M NaCl	Pure TTAB	TTAB-0.01M NaCl	Pure TTAB	TTAB-0.01M NaCl
293	0.710	0.80	0.56	0.51	2.94	3.28
298	0.708	0.71	0.59	0.54	2.80	3.06
303	0.704	0.71	0.63	0.60	2.65	2.78
308	0.703	0.71	0.63	0.61	2.65	2.74

7. Table 7: Absorption vs. Wavelength data of SRB for TTAB Surfactant.

Conc.(mM)	Pure TTAB		TTAB-0.01M NaCl		TTAB-0.05M NaCl	
	λmax	*Abs*	*λmax*	*Abs*	*λmax*	*abs*
1.25	-	-	-	-	516.0	0.0260
1.50	-	-	-	-	517.8	0.0820
1.75	-	-	-	-	520.8	0.1080
2.00	-	-	-	-	520.5	0.1334
2.25	-	-	-	-	520.0	0.1616
2.50	-	-	522.0	0.019	-	-
2.75	-	-	519.0	0.040	-	-
3.00	-	-	520.0	0.068	-	-
3.25	516.0	0.013	520.5	0.098	-	-
3.50	519.0	0.017	521.2	0.114	-	-
3.75	519.0	0.052	521.4	0.128	-	-
4.00	519.0	0.070	520.8	0.145	-	-
4.50	520.0	0.111	-	-	-	-
5.00	520.2	0.167	-	-	-	-

Table 8: By using the absorbance data and using the TTAB surfactant concentration it is the value of C_{surf} AND S_{mic}

Pure TTAB		**TTAB-0.01M NaCl**		**TTAB-0.05M NaCl**	
TTAB Conc (mM)-C_{surf}	**Sudan III (mM)-S_{mic}**	**TTAB Conc (mM)- C_{surf}**	**SudanIII (mM)-Smic**	**TTAB Conc (mM)-Csurf**	**Sudan III (mM)-Smic**
3.25	0.042	2.50	0.061	1.25	0.083
3.50	0.054	2.75	0.128	1.50	0.262
3.75	0.166	3.00	0.217	1.75	0.345
4.00	0.223	3.25	0.313	2.00	0.442
4.50	0.354	3.50	0.364	2.25	0.516
5.00	0.533	3.75	0.408	-	-
-	-	4.00	0.463	-	-

Table 9: MSR and Partition Coefficient (km) at 303k for TTAB

Conc. of Pure TTAB×10^3M	**Km**	**R^2**	**MSR**
3.25(CMC)	-	0.986	0.287×10^{-3}
3.50	1.73		
3.75	3.46		
4.00	5.19		
4.50	8.65		
5.00	12.11		

TTAB-0.05M NaCl	**Km**	**R^2**	**MSR**
Conc. Of TTAB×10^3M			
1.25 (CMC)	-		
1.50	1.20	0.97	0.42×10^{-3}
1.75	2.52		
2.00	3.78		
2.25	5.04		

TTAB-0.01M NaCl **Conc. Of TTAB×10^3M**	**Km**	**R^2**	**MSR**
2.50(CMC)	-		
2.75	1.12		
3.00	2.24		
3.25	3.36	0.98	0.27×10^{-3}
3.50	4.48		
3.75	5.60		
4.00	6.72		

Table 10:Krafft Temperature Measurement

Pure TTAB		**TTAB-0.01M NaCl**		**TTAB-0.005M NaCl**	
Temp/^{o}C	Conductance (mS/cm)	Temp/^{o}C	Conductance/(mS/cm)	Temp/^{o}C	Conductance(mS/cm)
5.0	320	5.0	1530	4.0	923
6.0	325	6.0	1531	5.0	923
7.0	332	7.0	1532	6.0	923
7.5	337	8.0	1533	7.0	923
8.0	342	8.5	1534	8.0	923
8.5	349	9.0	1535	9.0	927
9.0	356	9.5	1536	10.0	934
9.5	362	10.0	1545	10.5	950
10.0	369	10.5	1552	11.0	960
10.5	395	11.0	1557	12.0	962
11.0	415	11.5	1558	13.0	964
11.5	436	12.0	1559	14.0	966
12.0	443	12.5	1560	15.0	970
12.5	443	13.0	1562	16.0	976
13.0	443	14.0	1566	16.5	980
13.5	443	15.0	1570	17.0	983
14.0	443	-	-	-	-
14.5	443	-	-	-	-

Data of CTAB

Table1: Plot of conductance vs. Concentration of aqueous CTAB solution at different temperatures (293K; 298K; 303K; 308K)

CTAB Concentration /mM	Conductance /mS			
	298K	303K	308K	313K
0.2796	23.2	26.5	27	26.2
0.3642	31.3	34.1	34.2	34
0.4450	38.0	40.3	41.5	40
0.5223	45.4	47.8	48.5	47.5
0.5963	51.6	53.7	54.4	52.8
0.6672	57.0	59.1	60.2	58.7
0.7352	64.0	65.1	65.8	64.8
0.8010	69.5	70.5	71.2	70.4
0.8638	73.6	74.8	76.8	76.3
0.9240	78.7	79.5	81.6	81.8
0.9822	80.0	82.5	85.3	88
1.0380	81.2	83.6	86.4	89.3
1.0960	82.3	84.9	87.8	91
1.1480	83.3	86.1	89.1	92.3
1.1980	84.4	87.1	90.3	93.5
1.2460	85.5	88	91.3	94.8

Table 2 : Surface tension vs. Logarithm of the Concentrations of aqueous solutions of CTAB at different temperatures.

CTAB Concentration/mM	Log (C)	Surface Tension /mN/m			
		298K	303K	308K	313K
0.227	-3.644	61	61.3	62.2	63.9
0.297	-3.527	56	56.5	57.2	59.3
0.364	-3.439	52	53	53.4	55.2
0.424	-3.368	49	49.5	50.2	52
0.492	-3.308	46	47	47.8	49.2
0.553	-3.257	43.6	44.2	45	47.2
0.612	-3.213	41.4	42.2	43.3	45
0.668	-3.175	39.3	40.1	41.8	43.3
0.723	-3.141	38	39.1	40.3	41.8
0.776	-3.11	37	37.6	38.9	41
0.826	-3.08	36.4	36.8	38	40
0.877	-3.06	36	36.5	37.5	39
0.939	-3.027	35.7	36.4	37.2	38.2
0.985	-3.01	35.7	36.3	37	37.8
1.04	-2.98	35.7	36.3	37	37.5
1.09	-2.96	35.7	36.3	37	37.5
1.323	-2.94	35.7	36.3	37	37.5

Table3: CTAB-0.01m NaCl conductance vs. Concentration data at different temperatures

Conductance Data (μScm^{-1})									
CTAB conc (mM)	293K	CTAB conc. (mM)	298K	CTAB, Conc. mM	303K	CTAB, conc (mM)	308K	CTAB, conc (mM)	313K, (μS)
0.0784	1037	0.0784	1038	0.0784	1040	0.0784	1039	0.0784	1038
0.1162	1040	0.154	1043	0.154	1044	0.1162	1042	0.1162	1041
0.154	1044	0.227	1048	0.227	1048	0.154	1045	0.154	1044
0.1905	1048	0.297	1054	0.297	1052	0.1905	1048	0.1905	1047
0.227	1053	0.364	1061	0.364	1055	0.227	1051	0.227	1050
0.262	1056	0.429	1066	0.429	1058	0.262	1054	0.262	1053
0.297	1060	0.553	1076	0.553	1065	0.297	1057	0.297	1056
0.364	1067	0.612	1078	0.612	1068	0.364	1062	0.364	1061
0.429	1073	0.668	1079	0.668	1070	0.429	1066	0.429	1066
0.553	1075	0.723	1080	0.723	1071	0.522	1070	0.522	1069
0.612	1076	0.776	1081	0.776	1072	0.553	1071	0.5814	1071
0.668	1077	0.827	1082	0.827	1073	0.5814	1072	0.6389	1073
0.723	1078	0.877	1084	0.877	1074	0.612	1073	0.6945	1075
0.776	1079	0.939	1085	0.939	1075	0.6389	1074	0.7482	1077
-	-	0.985	1086	-	-	0.668	1075	0.8002	1079
-	-	-	-	-	-	0.6945	1076	0.8506	1081

Table: 4 Dependence of CMC Values Of (I) Pure CTAB (Ii) CTAB-0.01m NaCl on Temperatures

Temp (K)	CMC (mM) of Pure CTAB		Binding Constant (β)
	Surface Tension	Conductance	
298	0.83	0.92	0.80
303	0.83	0.94	0.70
308	0.87	0.97	0.67
313	0.94	0.98	0.66

Temp (K)	CMC of CTAB-0.01M NaCl		β, BindingConstant
	Surface tension	Conductance	
293	0.364	0.400	0.84
298	0.424	0.560	0.82
303	0.553	0.600	0.80
308	0.480	0.460	0.75
313	0.422	0.424	0.69

Table 5: Solubilizing Power (MSR) of CTAB solution in aqueous, 0.01m NaCl and 0.05 m NaCl systems at 303K.

Pure CTAB (aq)		CTAB-0.01M NaCl		CTAB-0.05M NaCl	
CTAB Conc (mM)	Sudan III (mM)	CTAB Conc (mM)	SudanIII (mM)	CTAB Conc (mM)	Sudan III (mM)
1.0	0.187	0.3	0.04	0.2	0.009
1.2	0.229	0.4	0.14	0.3	0.035
1.4	0.294	0.5	0.15	0.4	0.086
1.8	0.349	0.6	0.25	0.5	0.182
2.0	0.391	0.7	0.30	0.6	0.313
-	-	-	-	0.7	0.370
-	-	-	-	0.8	0.463

Table 6: Wavelength and Abs Data For Pure CTAB, CTAB-0.01M NaCl and CTAB-0.05M NaCl AT 303K

	Pure CTAB		CTAB-0.01M NaCl		CTAB-0.05M NaCl	
Conc.(mM)	**λmax**	**Abs**	**λmax**	**Abs**	**λmax**	**abs**
0.2	0	0	0	0	0	0
0.3	0	0	0	0	519	0.011
0.4	0	0	518.8	0.044	522	0.027
0.5	0	0	518.8	0.048	522	0.057
0.6	0	0	519.0	0.077	520	0.098
0.7	0	0	520.0	0.094	521	0.116
0.8	0	0	519.6	0.083	521	0.145
1.1	518.9	0.0586	-	-	-	-
1.3	519.2	0.0717	-	-	-	-
1.4	520.5	0.0920	-	-	-	-
1.8	521.0	0.1093	-	-	-	-
2	522.0	0.1227	-	-	-	-

Table 7: CTAB-0.01m NaCl Data from Surface Tension Measurement At Different Temperatures

Conc./mM	**Log(C)**	**293K**	**298K**	**303K**	**308K**	**313K**
0.154	-3.813	48.8	50.4	51.5	52.3	53.6
0.227	-3.644	40.5	42.7	44.0	45.0	46.3
0.297	-3.527	34.7	36.3	38.4	39.8	40.7
0.364	-3.439	30.8	32.4	34.6	35.9	37.1
0.424	-3.368	30.2	29.8	31.6	32.6	33.8
0.492	-3.308	30.0	29	29.3	29.6	33.0
0.553	-3.257	30.0	28.5	27.8	29.0	33.0
0.612	-3.213	30.0	28.5	27.0	29.0	33.0
0.668	-3.175	-	28.5	27.0	29.0	-
0.723	-3.141	-	28.5	27.0	29.0	-

Table8: Krafft Temperature For Pure CTAB (4mM) Solution

Pure CTAB		**CTAB (4mM)-0.01M NaCl**		**CTAB(4mM)-0.005M NaCl**	
Temp/^{o}C	Conductance(mS/cm)	Temp/^{o}C	Conductance(mS/cm)	Temp/^{o}C	Conductance,mS/cm
7.5	51.2	10	1205	8	550
8	52	11	1205	9	550
8.5	52.5	12	1205	10	550
9	53.2	13	1205	11	552
9.5	54	14	1206	12	554
10	54.8	15	1207	13	556
10.5	55.3	16	1209	14	560
11	56.1	16.3	1211	15	565
11.5	57	16.7	1215	16	570
12	57.5	17	1219	17	575
12.5	57.9	18	1221	18	584
13	59.9	18.5	1222	19	592
13.5	60.4	19	1224	19.5	598
14	61	19.5	1226	20	604
14.5	61.6	20	1228	21	617
15	62	21	1230	22	621
15.5	62.5	22	1232	23	623
16	63	23	1234	24	625
16.5	63.5	24	1236	25	628
17	64.7	25	1237	26	631
17.5	65.5	26	1238	27	634
18	66.6	27	1239	28	637
18.5	67.8	28	1240	29	639
19	69	29	1241	30	640
19.5	70	10	1205	8	550
20	71	30	1242	-	-
21	73.5	-	-	-	-
22	78.2	-	-	-	-
23	83.8	-	-	-	-
24	90.1	-	-	-	-
24.5	98.2	-	-	-	-
25	105.7	-	-	-	-
25.5	119.3	-	-	-	-
26	122.4	-	-	-	-
26.5	125.5	-	-	-	-
27	128	-	-	-	-
27.5	130.5	-	-	-	-
28.5	134	-	-	-	-

CALCULATION

Counter ion binding calculation: (from conductance data)

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

Example: in aqueous solution and in electrolyte solution the way of calculation of β is same.

At 293K in TTAB-0.01M NaCl solution

The value of post-micellar region = 16.956 (by taking the linear regression)

The value of pre-micellar region = 84.956 (by taking the linear regression)

Finally, $\alpha = \frac{16.956}{84.956} = 0.8004$

Note: In all temperatures and in all medium α values will be calculated in the same way.

Surface Excess Concentration: (from Surface Tension Data)

$$\Gamma = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln C}\right)_{T,P}$$

Example: In aqueous solution and in electrolyte solution the way of calculation of Γ is same

At 298K in CTAB-0.01M NaCl solution

The value of $(\frac{\partial \gamma}{\partial lnC}) = -45.29$ (from the slope of Surface Tension data in presence of 0.01M NaCl, calculated by linear regression)

$$\Gamma = \frac{1}{4.606} \times \frac{1}{8.314} \times \frac{1}{298} \times \frac{(-45.29)}{1000} = 3.9688$$

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

Thermodynamic parameters calculation for aqueous TTAB solution in different temperatures:

Mole fraction calculation:

At 293K, CMC = 3.4 mM, During this CMC value the total volume of the solution was (50+14)=64ml

We prepared,

250ml 1.5×10^{-2} M TTAB solution contains = 1.2615gm TTAB

14ml TTAB solution contains 0.070644gm TTAB

Mole of TTAB = $\frac{0.070644}{336.4} = 2.1 \times 10^{-4}$

Mole of water= 64/18=3.556

Mole fraction of TTAB in CMC= $2.1 \times 10^{-4}/(2.1 \times 10^{-4} + 3.556)$= 5.9057×10^{-5}

At, 293K, ln(CMC)= -9.737

Note: All the calculation for mole fraction has been calculated in the same way for TTAB and CTAB

Free Energy of Micellization (ΔG_m^o):

At 293K, $(G_m^o)_{293}$= (1+β) RT ln(CMC)= (1+0.697)×8.314×293× (-9.737)=-40.25 kJmol^{-1}

Note: All the calculation for Free Energy of Micellization (G_m^o) has been calculated in the same way for pure TTAB and CTAB solution.

Entropy Calculation (ΔS_m^o):

We know, $(\Delta S_m^o) = -\left\{\frac{\partial(\Delta G_m^o)}{\partial T}\right\}$

Now, plot the (ΔG_m^o) vs. T for pure TTAB solution in excel sheet and we get an equation like

$$(\Delta G_m^o) = 1.14T^2 - 791.58T$$

$$\frac{\partial(\Delta G_m^o)}{\partial T} = 1.14 \times 2 \times T - 791.58$$

So for $T = 293K$, $(\Delta S_m^o) = -\left\{\frac{\partial(\Delta G_m^o)}{\partial T}\right\} = 123.54$

Note: we can calculate the value of (ΔS_m^o) in each temperature for pure TTAB and CTAB solution.

Enthalpy Calculation:

We know, $\Delta G_m^o = \Delta H_m^o - TS_m^o$

At 293K, $TS_m^o = 123.54 \times \frac{293}{1000} = 36.197 kJmol^{-1}$, Here $\Delta G_m^o = -40.25 kJmol^{-1}$

So, $\Delta H_m^o = -4.062 kJmol^{-1}$

Note: we can calculate the value of ΔH_m^o in each temperature for pure TTAB and CTAB solution.

Thermodynamic parameters calculation for aqueous TTAB-0.01M NaCl solution at different temperatures:

Mole fraction calculation:

At 293K, the CMC = 2.64 mM

During this CMC, the total volume of solution (water+TTAB+NaCl) is = 60.5 ml

1000 ml 0.01M NaCl solution contains 0.584428gm

60.5 ml 0.01 M NaCl solution contains 0.03534 gm

Mole of NaCl= $\frac{0.03534}{58.4428}$= 6.045×10^{-4}

Mole of TTAB (calculated on the same way) = 1.575×10^{-4}

Mole of Water = 3.361

Total Mole (water+TTAB+NaCl) = 3.36176

Mole fraction of TTAB in CMC (X_{cmc}) = $\frac{Mole\ of\ TTAB}{Total\ Mole} = 4.685 \times 10^{-5}$

Mole fraction of NaCl salt $(X_s) = \frac{Mole of\ NaCl}{Total\ Mole} = 1.798 \times 10^{-4}$

Free Energy Calculation in presence of 0.01M NaCl of TTAB solution:

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

We will get all the value from the previous calculation. Here α is degree of ionization of TTAB in presence of 0.01M NaCl. So, α =0.1996

By putting all the value, $\Delta G_m^0 = -40.647 kJmol^{-1}K^{-1}$

Note: ΔG_m^0 values for all temperature should be calculated in same way.

Entropy Calculation inin presence of 0.01M NaCl of TTAB solution:

Follow the same calculation of Entropy of pure TTAB calculation.

Enthalpy Calculation in in presence of 0.01M NaCl of TTAB solution:

Follow the same calculation of Entropy of pure TTAB calculation.

Calculation of MSR and Partition Coefficient (Km) at 303K for TTAB

MSR= Molar Solubilization Ratio

Km = Partition Co-efficient

$$(\mathbf{Smic} - \mathbf{Scmc}) = \mathbf{MSR}(\mathbf{Csurf} - \mathbf{Ccmc}) \quad \text{---------- (1)}$$

From this equation MSR represents a slope for a specific surfactant solution

$$\mathbf{Km} = \frac{\mathbf{MSR}(\mathbf{X} - \mathbf{Xo})}{\mathbf{Vo}} \quad \text{---------- (2)}$$

For Pure TTAB:

Here, X = concentration of surfactant above the CMC

Xo = Concentration of surfactant at CMC = 3.25 mM

Yo = Concentration of Sudan Red B at CMC = 0.0415×10^{-6}

S_{mic}= Total solubility of the solute in micelle at the surfactant concentration higher than the CMC

C_{surf}= The surfactant at the $S_{mic}$is evaluated.

S_{cmc} = the solubility of organic solute in mole per liter at the CMC = 0.0415×10^{-6}

C_{cmc} = Concentration at the CMC = 3.25 mM

We have got the extinction coefficient (ε) of sudan red B is 0.3134

Beer-Lambert low, we know, $A = \varepsilon bC$……(3)

Here, A= Absorbance, b = length of the passing path through the cell, C= Concentration of the solubilized dye.

From data, we get at 303K, when TTAB concentration is 3.25mM, sudan red B give the absorbency = 0.013 and corresponding wave length = 516.

So, from the equation, we get, Concentration of Sudan Red B at CMC = 0.0415×10^{-6}

Note: By using the absorbency from data table and the equation (3) we can get all the values of concentration of sudan red B with the corresponding surfactant concentration.

MSR Calculation:

$$(S_{mic} - S_{cmc}) = \mathbf{MSR}(C_{surf} - C_{cmc})$$

For example, when $C_{surf} = 3.5 \times 10^{-3} M$, the value of $(C_{surf} - C_{cmc}) = 0.25 \times 10^{-3} M$

And, $S_{mic} = 0.0542 \times 10^{-6}$, it is calculated by using the equation (3) please see above

The value of $(S_{mic} - S_{cmc}) = 0.0127 \times 10^{-6} M$

By following the calculation we will calculate all the calculation from the table of Concentration vs. absorbance data. If we plot all the data of $(S_{mic} - S_{cmc})$ **in Y-axis** and the data of $(C_{surf} - C_{cmc})$ **in X-axis, we** will get a slope from linear regression. This slope indicates the value of **Molar Solubilization Ratio** (**MSR**).

Partition Coefficient calculation:

$$K_m = \frac{\mathbf{MSR}(C_{surf} - C_{cmc})}{S_{cmc}}$$

From the above data, we can find the Partition coefficient value K_m from eachcorresponding surfactant concentration.

Calculation of Aggregation number (N_{agg}):

$$\left(\frac{\Lambda_o - \Lambda}{\Lambda_o - \Lambda_{cmc}}\right)^2 = 1 - \frac{\beta(1+n\beta)}{2} + \frac{\beta(1+n\beta)}{2}\left(\frac{C}{C_{cmc}}\right) \quad \text{.....(1)}$$

$$\left(\frac{\Lambda_o - \Lambda}{\Lambda_o - \Lambda_{cmc}}\right)^2 = 1 - \frac{\beta(1+n\beta)}{2}\left\{1 - \left(\frac{C}{C_{cmc}}\right)\right\} \quad \text{.....(2)}$$

We know, $\Lambda = \Lambda_o + a\sqrt{C}$, here $\Lambda = \frac{\kappa}{C}$ and plot the value of Λ in **Y-axis (axis range 60-120) and** $\sqrt{C}$ in **X-axis (keep away first 5-6 data during plotting to find out the intercept).**

After plotting the value, we will get an intersection point after extrapolating the graph, the intersection point is Λ_o.

Now, again plotting the $\left(\frac{\Lambda_o - \Lambda}{\Lambda_o - \Lambda_{cmc}}\right)^2$ in Y-axis and $\left\{1 - \left(\frac{C}{C_{cmc}}\right)\right\}$ in X-axis we will get a slope from the linear portion.

Now, slope = $\frac{\beta(1+n\beta)}{2}$ ……..(3)

Here β is degree of ionization and n is the aggregation number. By using the equation 3, we will find out the value of n.